Cambridge (CIE) A Level Chemistry

Your notes

Characteristic Organic Reactions

Contents

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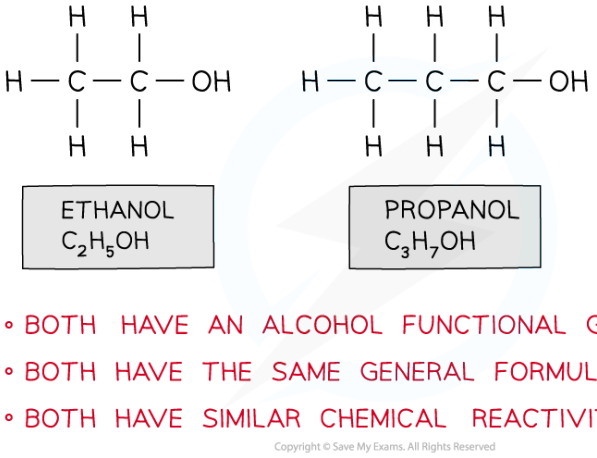
Definitions & Terminology in Organic Chemistry

Homologous series

- A homologous series is a group of organic compounds that have the same functional group, the same general formula and the same chemical properties

The homologous series of alcohols

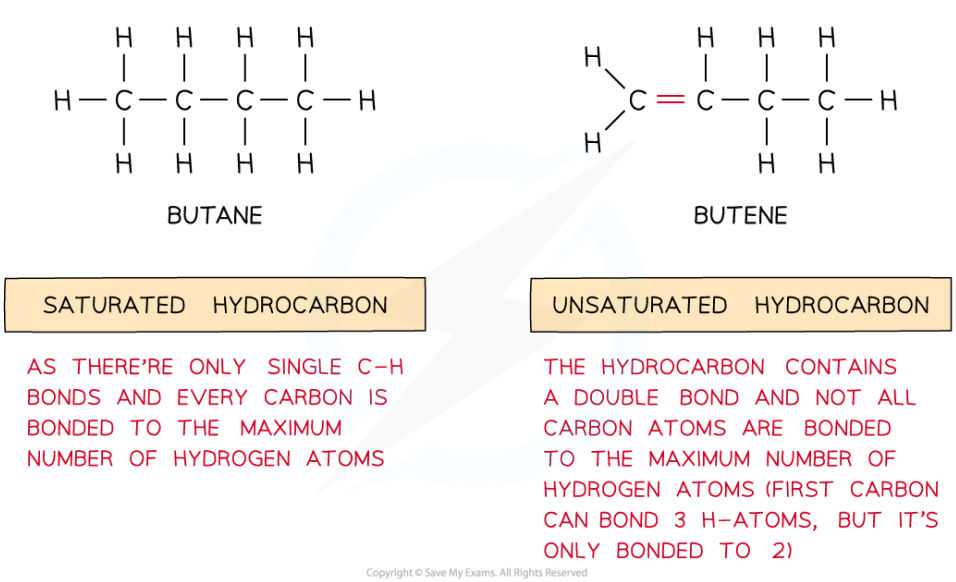


Ethanol and propanol belong to the same homologous series

Saturated & unsaturated hydrocarbons

- **Saturated** hydrocarbons are hydrocarbons which contain single bonds only resulting in the maximum number of hydrogen atoms in the molecule
- **Unsaturated** hydrocarbons are hydrocarbons which contain carbon-carbon **double** or **triple** bonds

Comparing the alkane and alkene homologous series



The diagram shows saturated hydrocarbons which contain single bonds only and unsaturated hydrocarbons which contain double/triple bonds as well

Homolytic & heterolytic fission

- **Homolytic fission** is breaking a covalent bond in such a way that each atom takes an electron from the bond to form two radicals
- **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

Examples of homolytic & heterolytic fission

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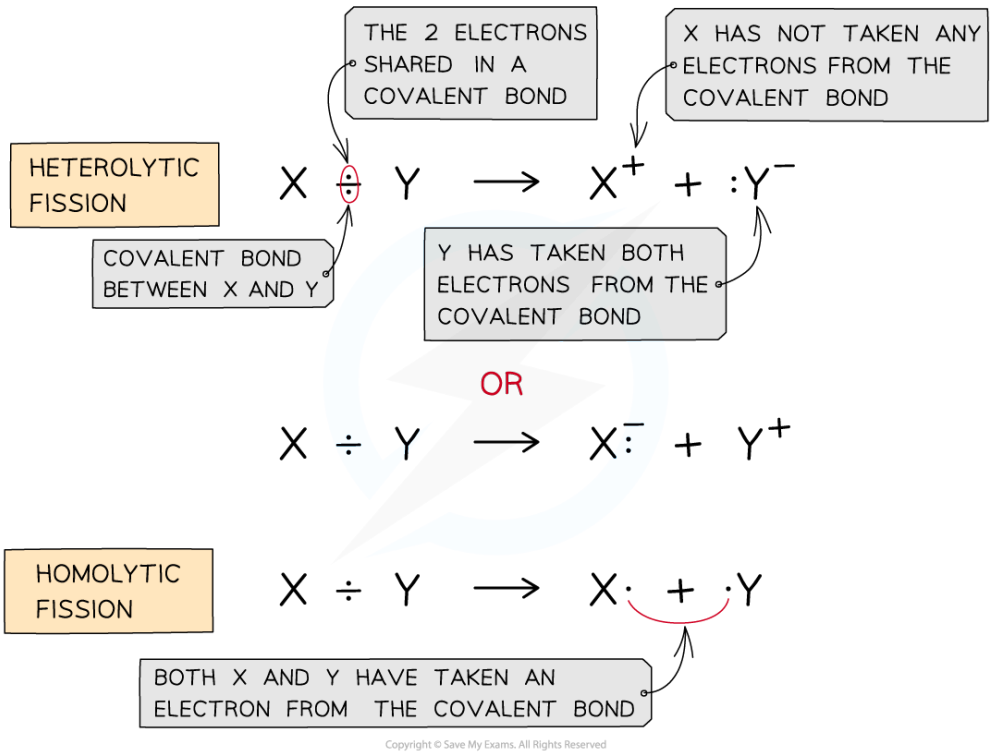
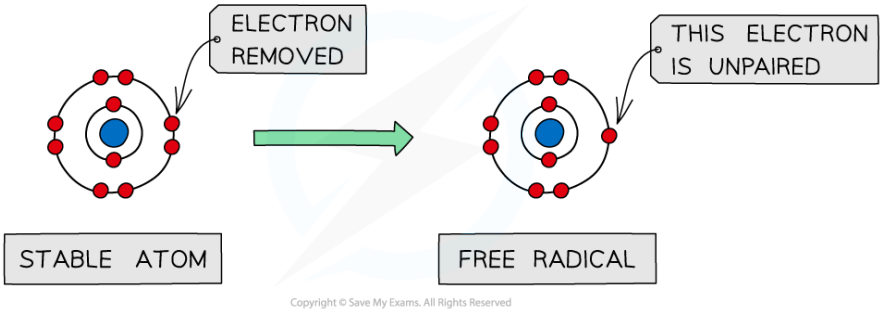


In heterolytic fission, the most electronegative atom takes both electrons in the covalent bond. While in homolytic fission, each atom takes one electron from the covalent bond

Radical chain reactions

- A **free radical** is a species with one (or more than one) unpaired electrons

Free radicals



The diagram shows a free radical which has one unpaired electron

- A **free radical reaction** is a reaction involving free radicals and is a three-step reaction:
  - **Initiation** is the first step and involves breaking a covalent bond using energy from ultraviolet (UV) light from the sun to form two free radicals
  - The **propagation** step is the second step in which the formed radical can attack reactant molecules to form even more radicals

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- These in turn can again attack other molecules to form more free radicals and so on
- In the **termination** step, two free radicals react together to form a product molecule

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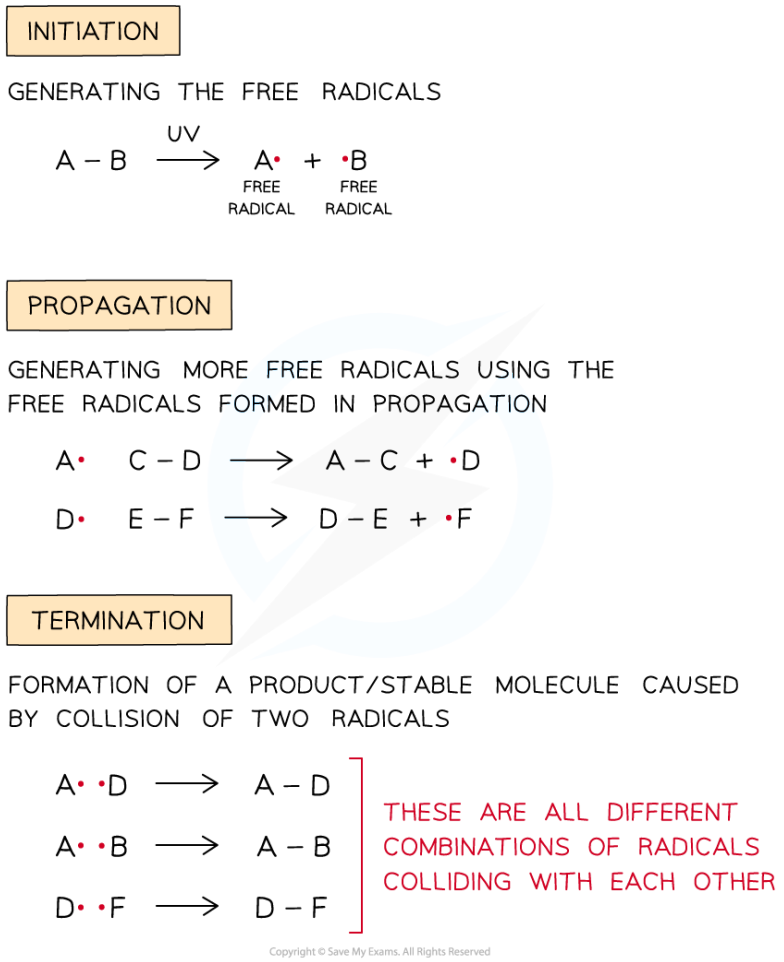
The steps of a free radical reaction mechanism

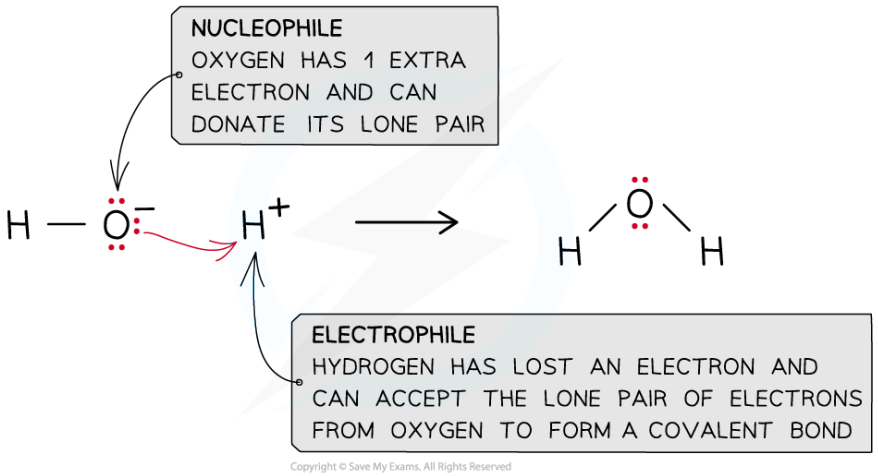


The main steps of a free radical reaction mechanism are initiation, propagation and termination

Nucleophiles & electrophiles

- 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
- An **electrophile** is an electron-deficient species that can **accept** a pair of electrons
  - 'Electrophile' means 'electron/negative charge loving' as electrophiles are attracted to negatively charged species
  - **Electrophilic** refers to reactions that involve an electrophile

Examples of a nucleophile and an electrophile



A nucleophile 'loves' a positive charge and an electrophile 'loves' a negative charge

Types of reactions

- An **addition** reaction is an organic reaction in which two (or more) molecules combine to give a **single product** with no other products
- A **substitution** reaction is a reaction that involves **replacing** an atom or group of atoms with another atom or group of atoms
- An **elimination** reaction is a reaction in which a small molecule (such as H_2O or HCl) is **removed** from an organic molecule
- A **hydrolysis** reaction is a reaction in which a compound is **broken down** by **water** (it can also refer to the breakdown of a substance by dilute acids or alkalis)
- A **condensation** reaction is a reaction in which two organic molecules join together and in the process **eliminate** small molecules (such as H_2O or HCl)

The different types of reactions in organic chemistry

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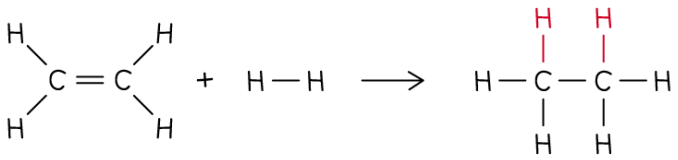
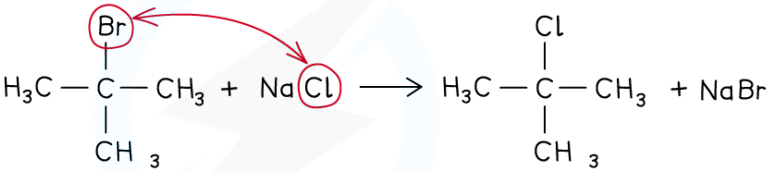
ADDITION REACTION



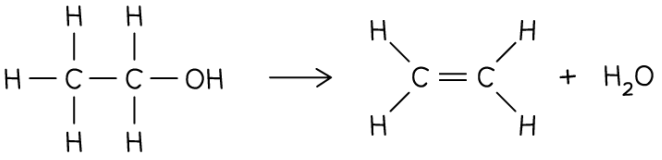
ADDITION OF H_2 TO THE DOUBLE BOND IN ETHENE TO GIVE A SINGLE PRODUCT ETHANE

SUBSTITUTION REACTION



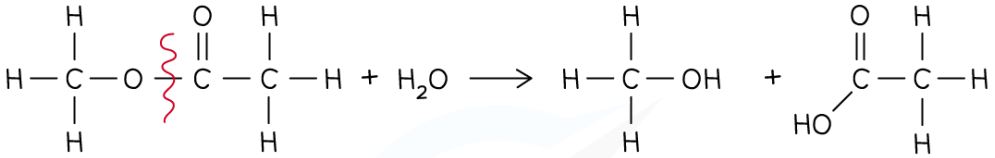
CHLORINE HAS REPLACED BROMINE

ELIMINATION REACTION



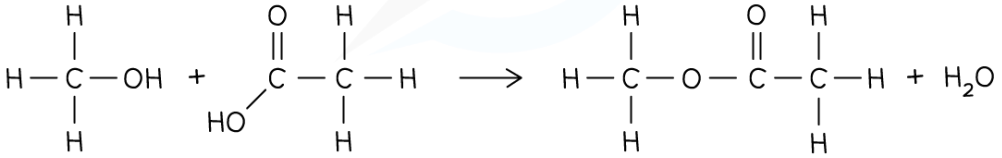
H_2O (SMALL MOLECULE) HAS BEEN REMOVED

HYDROLYSIS



WATER HAS BEEN USED TO BREAK DOWN THE ESTER INTO AN ALCOHOL AND A CARBOXYLIC ACID

CONDENSATION REACTION



TWO ORGANIC MOLECULES (ALCOHOL AND CABROXYLIC ACID) REACT TOGETHER AND ELIMINATE A SMALL MOLECULE (H_2O)

It is important to be able to describe and identify the different types of reaction in organic chemistry

Oxidation & reduction

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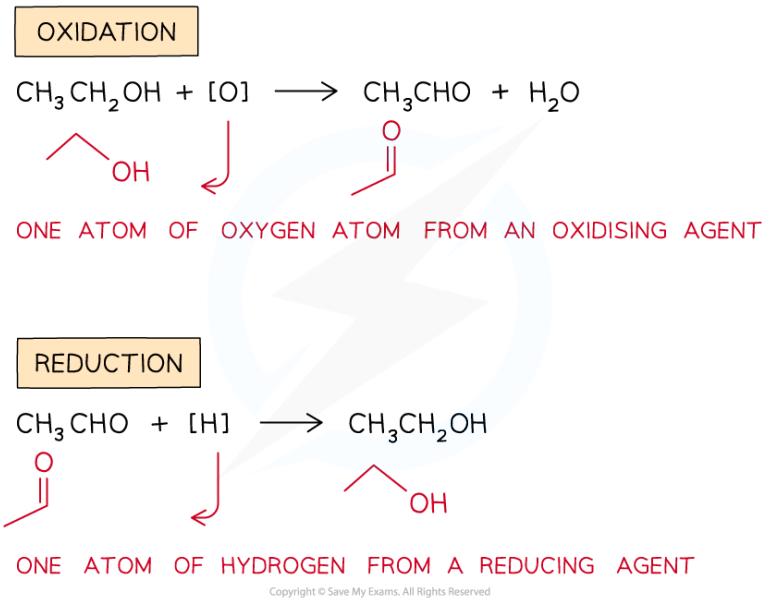
- An **oxidation** reaction is a reaction in which oxygen is added, electrons are removed or the oxidation number of a substance is increased
  - In organic chemistry, it often refers to the **addition of oxygen** or removal of hydrogen atoms to a substance
  - In equations for organic redox reactions, the symbol **[O]** can be used to represent one atom of oxygen from an oxidising agent
- A **reduction** reaction is a reaction in which oxygen is removed, electrons are added or the oxidation number of a substance is decreased
  - In organic chemistry, it often refers to the **removal of oxygen** or addition of hydrogen atoms to a substance
  - In equations for organic redox reactions, the symbol **[H]** can be used to represent one atom of hydrogen from a reducing agent

Examples of oxidation and reduction



In organic chemistry oxidation is often the gain of oxygen or loss of hydrogen atoms and reduction is the gain of hydrogen and loss of oxygen atoms

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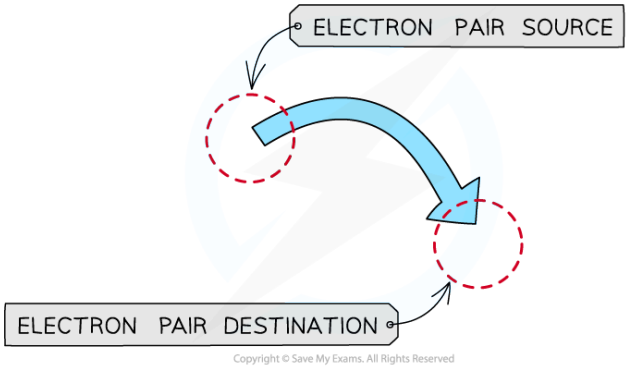
Terminology Used in Reaction Mechanisms

- In organic reaction mechanisms, **curly arrows** represent the movement of **electron pairs**
- The arrow begins at a bond or a lone pair of electrons and points to the species that accepts the lone pair of electrons

An organic mechanism curly arrow



Curly arrows show electron pairs moving from the source (eg. a nucleophile) to its destination (eg. an electrophile)

Free-radical substitution

- A **free-radical substitution reaction** is a reaction in which halogen atoms substitute for hydrogen atoms in alkanes
- Free radical substitution involves three standard steps:
  - Initiation
  - Propagation
  - Termination

Initiation step

- The covalent Cl-Cl bond is broken by energy from the UV light
- Each atom takes **one electron** from the covalent bond
- This produces two radicals in a **homolytic fission** reaction

$$Cl{-}Cl \rightarrow 2Cl^{\bullet}$$

Propagation step

- The halogen free radicals are very reactive and will attack the unreactive alkanes

- One of the methane C-H bond breaks homolytically to produce an alkyl radical

$$CH_4 + Cl^\bullet \rightarrow {}^\bullet CH_3 + HCl$$

- The alkyl radical can attack another chlorine molecule to form a halogenoalkane
- This also regenerates the chlorine free radical

$$^\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$$

- The regenerated chlorine free radical can then repeat the cycle

Termination step

- Multiple products are possible, dependent on the radicals involved
  - They are commonly classed as desirable (wanted) and undesirable (unwanted)
- In the single substitution of methane with chlorine:
  - Chloromethane is the desirable (wanted) product:

$$^\bullet CH_3 + Cl^\bullet \rightarrow CH_3Cl$$

- Ethane and chlorine are undesirable (unwanted) products:

$$^\bullet CH_3 + {}^\bullet CH_3 \rightarrow CH_3CH_3$$

$$Cl^\bullet + Cl^\bullet \rightarrow Cl_2$$

Electrophilic addition

- An **electrophilic addition** reaction is a reaction in which an electron rich region in a molecule is attacked by an electrophile (a species that likes electrons/negative charge) followed by the addition of a small molecule to give one product only

Example of an electrophilic addition reaction to form ethanol from ethene

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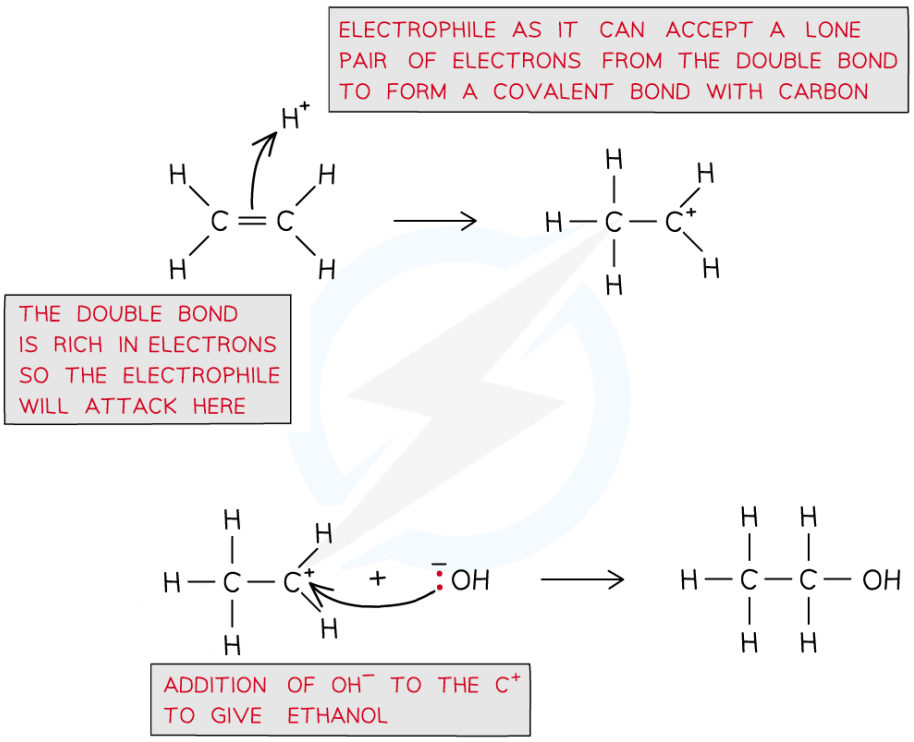
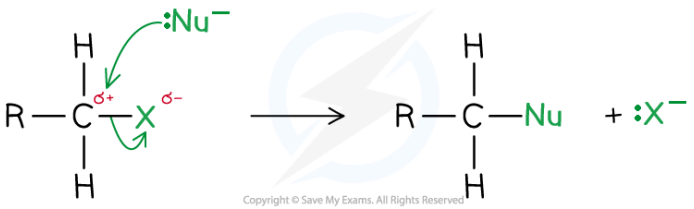


Curly arrows always move from an area of high electron density to an area of low electron density

Nucleophilic substitution

- A **nucleophilic substitution** reaction is a reaction in which an electron-rich nucleophile **displaces** a halogen atom

The general nucleophilic substitution reaction mechanism



In nucleophilic substitution reaction mechanisms, the nucleophile replaces an atom / group in the target molecule

- The C-X carbon of the halogenoalkane is electron deficient and has a δ+ charge
  - The halogen atom, X, is more electronegative than the carbon atom which means that it pulls electrons towards itself and is δ−
- The nucleophile has a lone pair of electrons that it can donate to the δ+ carbon atom and form a covalent bond
- This causes the displacement of the halogen atom, X, which leaves as a halide ion, X^-

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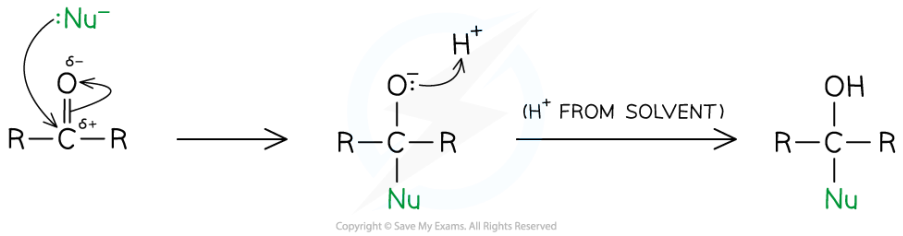
- The displaced halide ion is known as a **leaving group**

Nucleophilic addition

- A **nucleophilic addition** reaction is a reaction in which a nucleophile (a species that likes a nucleus/positive charge) attacks an electron-deficient region in a molecule followed by the addition of a small molecule to give one product only

The general nucleophilic addition reaction mechanism



In nucleophilic addition reaction mechanisms, the nucleophile is added to the target molecule

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