

REACTION MECHANISMS

Reaction Classification

The table below reviews the organic reactions studied for AS chemistry, how they are classified and the reaction mechanisms where required.

Reaction	Reaction classification	Reaction mechanism
Alkane and halogen	Substitution	Free radical substitution
Alkene and H ₂	Addition (reduction)	
Alkene and halogen and HBr	Addition	Electrophilic addition (Br ₂)
Alkene and hydrogen halide	Addition	Electrophilic addition (HBr)
Alkene and KMnO ₄	Oxidation	
Alkene polymerization	Polymerization	
Alcohol with H ₂ SO _{4(aq)} and K ₂ Cr ₂ O ₇	Oxidation	
Alcohol with halogenating agents	Substitution	Nucleophilic substitution
Halogenoalkanes and KOH _(aq)	Substitution	Nucleophilic substitution
Halogenoalkanes and KOH _(eth)	Elimination	
Halogenoalkanes and water	Substitution / Hydrolysis	Nucleophilic substitution

Free radical reactions

A typical example of these is between an alkane and a halogen.

e.g. methane and chlorine. They involve an attack by an atom or group with an unpaired electron called a free radical. In the above reaction ultraviolet light causes chlorine atoms (free radicals) to form, Cl· and methyl radicals, CH₃· are also involved. The dot shows the unpaired electron.

Electrophilic addition reactions

A typical example of these is between an alkene and a hydrogen halide. e.g. ethene and hydrogen bromide. They involve an attack by an ion or group with a positive or partial positive charge called an electrophile. In the above reaction the electrophile is a hydrogen ion H⁺. Electrophiles attack centres of negative charge like the electrons in a double bond. These are addition reactions because the two reactants are added together to give one product.



Nucleophilic substitution reactions

A typical example of these is between an alcohol and hydroxide ions. e.g. ethanol and aqueous sodium hydroxide. They involve an attack by an ion or group with a negative or partial negative charge called a nucleophile. In the above reaction the hydroxide ion OH⁻ is the nucleophile.

A nucleophile attacks a centre of positive charge such as the partial positive charge on the carbon atom holding a halogen C^{δ+}-X. It is a substitution reaction because the attacking species replaces the species originally attached to the carbon atom under attack.



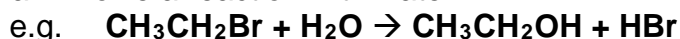
Elimination reactions

A typical example is the formation of an alkene from an alcohol. E.g. Ethanol reacting to form ethene. They involve atoms or groups from either side of a single carbon to carbon bond being removed (eliminated) to form a double bond.



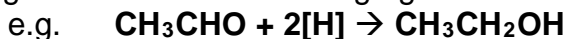
Hydrolysis reactions

These all involve a reaction with water.



Reduction reactions

These involve a reaction with hydrogen. A compound gains hydrogen. This can be hydrogen H_2 or from a reducing agent like LiAlH_4 in ether or aqueous NaBH_4 .



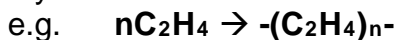
Oxidation reactions

These reactions involve the loss of hydrogen or the gain of oxygen. An oxidising agent like acidified potassium dichromate (VI) is used.



Polymerisation reactions

These reactions involve the joining of small molecules called monomers to make large molecules called polymers. A large number (n) of monomer molecules is involved and a long polymer molecule is formed.



Classification of Reagents

Chemists aim to develop a systematic approach to chemical reactions. In order to do this for organic chemistry it is useful to classify types of compound and how they behave. It is also useful to classify reagents so that predictions can be made about the most effective way of carrying out a new reaction.

Reagents can be classified in various ways including **oxidising agents**, **reducing agents** and **chlorinating agents**.

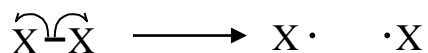
Bond Breaking and Reaction Mechanisms

Reaction mechanisms were introduced in Unit 1 as the study of the step by step processes involved in a reaction.

All reaction mechanisms involve looking at bond breaking.

There are two ways in which bond breaking takes place; **homolytic** and **heterolytic**.

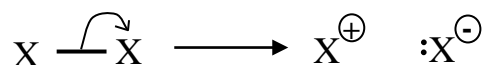
In a **homolytic process**, the bond breaks so that the atoms on each side of the bond being broken receive one of the electrons from the bonding pair.



The single headed curly arrows represent the movement of one electron.

Homolytic fission involves the formation of radicals. A radical is an atom or group of atoms with an unpaired electron.

In a heterolytic fission process, the bond does not split the electrons evenly, but both electrons go to one of the atoms on one side of the bond.



The species formed by this process are ions; a **cation** and an **anion**.

The cation, because of the positive charge, will be attracted to a region of negative charge. It has a vacancy for two electrons, so it tends to accept an electron from another atom and form a bond. Such a species is called a **nucleophile**. A carbon atom possessing a positive charge is called a carbocation.

The anion, because of the negative charge, will be attracted to a region of positive charge. It has two electrons available, so it tends to donate an electron to another atom and form a bond. Such a species is called an **electrophile**. A carbon atom possessing a negative charge is called a carbanion.

Definitions

Three important definitions are given here.

Free radical - A free radical an atom or group of atoms with an unpaired electron.

Nucleophile - A nucleophile is a species attracted to a region of positive charge and is an electron pair donor.

Electrophile - An electrophile is a species attracted to a region of negative charge and is an electron pair acceptor.

Bond type and Reaction Mechanism

The nature of bond present in a compound will determine what type of mechanism takes place in a reaction.

A halogenoalkane, for example, will have a polar bond because of the electronegativity of the halogen. This leaves the carbon bonded to the halogen with a partial positive charge. This makes the carbon with the partial positive charge susceptible to nucleophilic attack.

Alkenes have a double bond which has a high electron density. The high electron density creates a region of higher negative charge and so invites electrophilic attack.

Reaction Mechanisms

The following reaction mechanisms have been studied in Unit 1:

- The reaction of methane with chlorine
- The reaction of bromine and hydrogen bromide with ethene
- The reaction of hydrogen bromide with propene

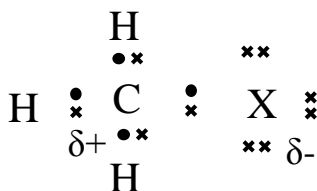
Mechanisms in Unit 2

Substitution reaction in halogenoalkanes

Halogens are electronegative and draw electrons away from the carbon atom leaving it with a partial positive charge. This is susceptible to attack by a nucleophile. There are two different nucleophilic substitution mechanisms.

With primary halogenoalkanes the nucleophile approaches the carbon atom and begins to form a bond. At the same time the bond with the halogen begins to break, with both electrons in the bonding pair going to the halogen.

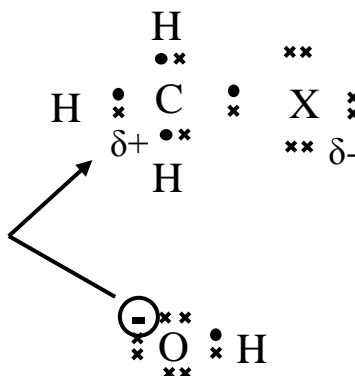
Looking at dot and cross diagram for the reaction. This is not the way the mechanism is shown.

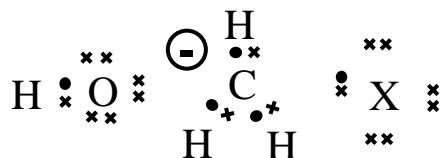


1. The halogen in the halogenoalkane is electronegative so draws the bonding electron pair towards itself and creating a partial positive charge on the carbon.

2. The partial positive charge on the carbon invites attack of nucleophiles such as a hydroxide ion.

3. The hydroxide ion donates an electron pair to the carbon and starts to form a bond.

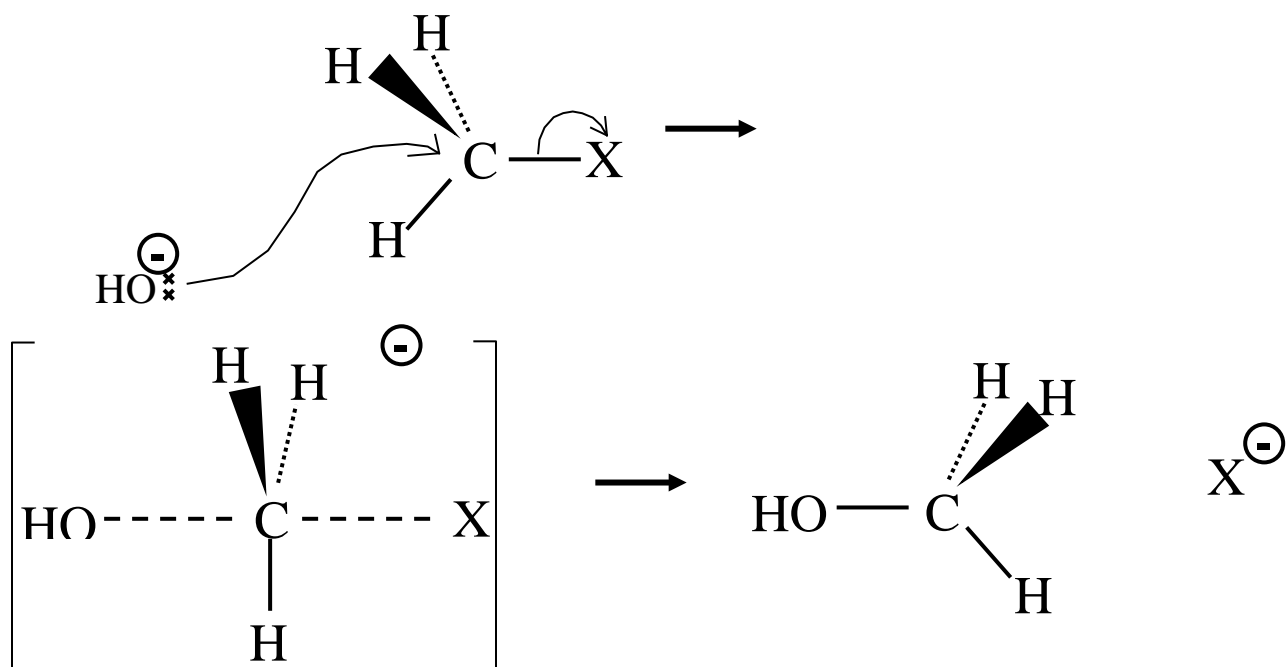




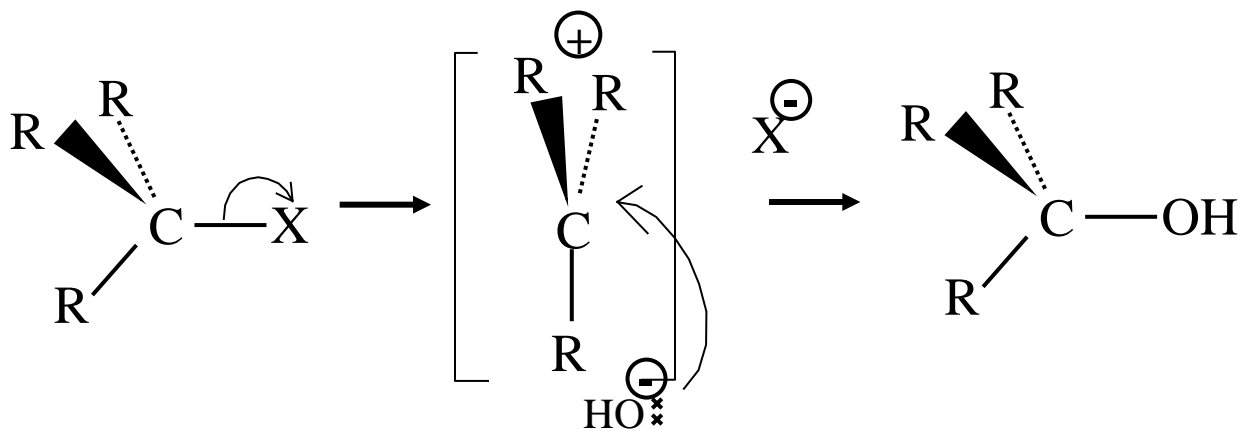
4. An intermediate is formed with the C-O bond forming and the C-X bond breaking.

This reaction involves **two** species (the halogenoalkane molecule and hydroxide ion) in the slow (bond breaking) step and is designated **$\text{S}_{\text{N}}2$** .

The mechanism is shown as follows;



With tertiary halogenoalkanes, the carbon groups around the carbon with the halogen attached stabilise the ion, so allowing the ion to form. Once the ion has been formed the hydroxide ion can join in place of the halogen. The intermediate formed, the **carbocation**, is planar, so the hydroxide ion can attack from either side.



If the hydroxide ion attacked from the opposite side from that shown, the product would be the mirror image of the molecule above.

In these reactions, the slow step is the breaking off of the halogen and this involves only the halogenoalkane, that is one species, and it is designated **S_N1**.

Independent research

Research the formation of ozone in the upper atmosphere, the free radical reaction mechanisms involved in the breakdown of this ozone and the part played by aircraft emission of nitrogen oxides.