Chem Factsheet

Reaction Mechanisms

To succeed in this topic you need to:

- Have a good knowledge of the AS and A2 level organic chemistry reactions covered so far;
- Be confident in using organic terminology, nomenclature and structural formulae.

After working through this Factsheet you will:

- Be able to represent movement of electron using the "curly arrow" convention;
- Have been shown the key reaction mechanisms.

All chemical reactions involve the movement of electrons, and reaction mechanisms allow us to display these movements and understand more about how a reaction occurs.

In this Factsheet you will meet organic reactions which you have come across before. You should already be able to recall the overall reaction equations and conditions required. The reaction mechanisms, which also require learning, often split these reactions up into several steps, each step involving the movement of electrons. This should give an insight into how a reaction occurs.

You need to be able to represent the movement of electrons using the "curly arrow" convention:

     represents the movement of an electron **pair**

     represents the movement of a **single** electron.

When using curly arrows it is vital that you position each end of the arrows carefully, so that you clearly show the examiner that you know where the electrons are moving **from** and **to**.
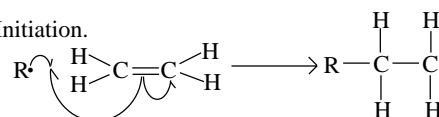
> **Exam Hint: -** *Reaction mechanisms are commonly examined. As well as learning the standard examples given here, you need to practise applying the mechanisms to other similar reactions.*

2. Homolytic Free Radical Addition.
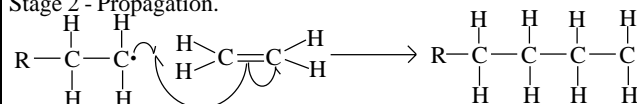
Example: Polymerisation of ethene.

The initiator is a free radical, R• (which could be a peroxide radical from the oxygen catalyst).
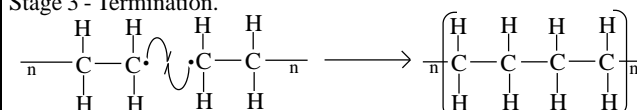
Stage 1 - Initiation.

The new radical formed can then react with further ethene molecules to lengthen the polymer chain.

Stage 2 - Propagation.

Termination can occur when two radical chains meet, or when a radical chain attacks an established chain.

Stage 3 - Termination.

The end product, polyethene, consists of long chain molecules (of varying length) which are branched.
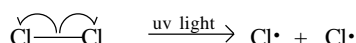
1. Homolytic Free Radical Substitution

These reactions involve **free radicals**, very reactive species which have a single, unpaired electron.
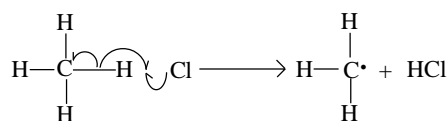
Example: Alkanes with chlorine.

The reaction between methane and chlorine occurs in 3 stages.

Stage 1 - Initiation

$$Cl \text{—} Cl \xrightarrow{\text{uv light}} Cl\bullet \ + \ Cl\bullet$$

The Cl-Cl bond is broken homolytically to form two chlorine free radicals. Energy is required to break the bond, hence the reaction only begins in the presence of UV light.
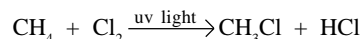
Stage 2 - Propagation

Any such reaction caused by a free radical, where "replacement" free radicals are produced by the reaction, hence the reaction process continues unaided.
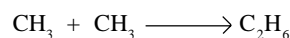
Stage 3 - Termination
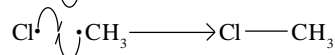
Free radicals are used up and not regenerated, causing the reaction to eventually stop.

The overall reaction equation is as follows:

$$CH_4 \ + \ Cl_2 \xrightarrow{\text{uv light}} CH_3Cl \ + \ HCl$$

But be aware that "by-products" are also formed in such reactions, e.g. the formation of ethane (when chloromethane is the target molecule).
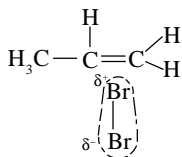
$$CH_3 \ + \ CH_3 \longrightarrow C_2H_6$$

Most free radical reactions are extremely unstable and explosive. This reaction between methane and chlorine is controlled using subdued UV light.

3. Heterolytic Electrophylic Addition

Example: Alkenes with halogens or hydrogen halides.

Consider the addition of bromine to propene.

The electrons in the double bond repel the electrons in the approaching Br_2 molecule, causing a dipole.

The δ^+ end of the halogen molecule is electrophilic, and can attack the electron rich π-bond.

Meanwhile, the δ^- end of the halogen molecule will accept both of the bond pair of electrons, forming a negative anion.
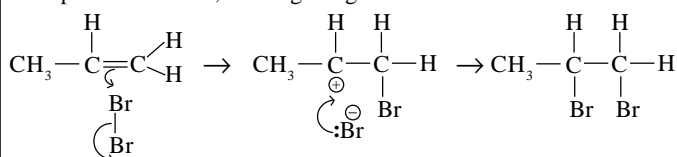
Note the formation of a carbocation ($C^{\oplus}$) intermediate. The most stable position for the carbocation will be the carbon with the least hydrogen atoms around it.

hence was formed, **not**
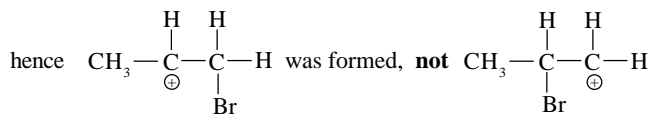
There is a similar reaction mechanism for the addition of hydrogen halides to alkenes.
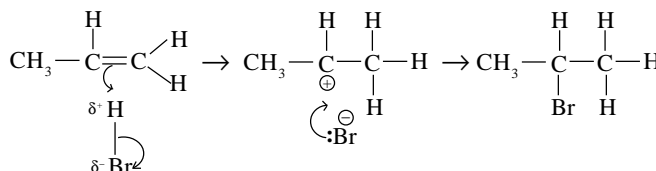
Markownikov's Rule
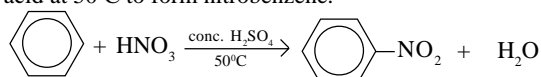When a hydrogen halide is added to a C=C double bond, the hydrogen atom is added to the carbon atom that already carries more hydrogens.

4. Heterolytic Electrophilic Substitution

Examples: Reactions of benzene (see Chem Factsheet 39).

(a) Nitration of benzene

Benzene reacts with a mixture of conc. nitric acid and conc. sulphuric acid at 50°C to form nitrobenzene.
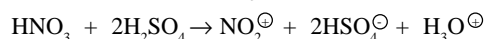

The reaction of benzene with nitric acid alone is slow and pure sulphuric acid at 50^0C has little or no effect on benzene.

Therefore, sulphuric acid must react with nitric acid forming a species which **will** attack the benzene ring.
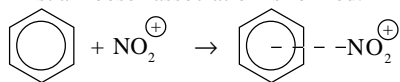
Evidence suggests that this is the $NO_2^{\oplus}$ species - an electrophile formed by the removal of $OH^{\ominus}$ from HNO_3:

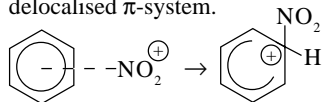$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^{\oplus} + 2HSO_4^{\ominus} + H_3O^{\oplus}$$

Note that the nitric acid is acting as a base (proton acceptor) in the presence of a stronger acid.

The $NO_2^{\oplus}$ ion is a strong electrophile, so attacks the delocalised π-electron system in the benzene ring.

First a "loose" association is formed.

NO_2^+ then attacks a C atom, forming a bond and distrupting the delocalised π-system.

Note that a considerable amount of energy is required to disrupt the very stable π-system, therefore this step has a very high activation energy.
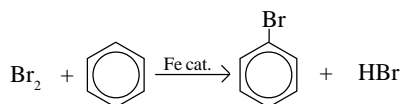
The intermediate cation will then break down to either reform benzene, or form nitrobenzene.

The delocalised system reforms, hence energy is released.
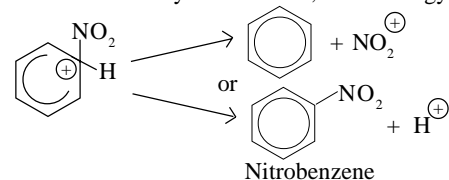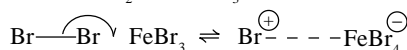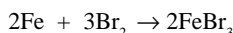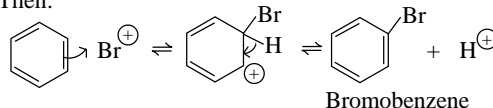

(b) Bromination of benzene

Bromine reacts with benzene in the presence of an iron wire catalyst in dry conditions at room temperature.

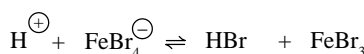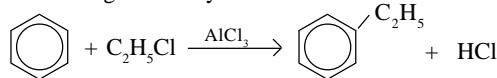The electrophile Br^+ must be generated to attack the benzene ring.

$$2Fe + 3Br_2 \rightarrow 2FeBr_3$$

Then:

Bromobenzene is formed and the $H^{\oplus}$ is the removed by $FeBr_4^{\ominus}$ to regenerate the $FeBr_3$.
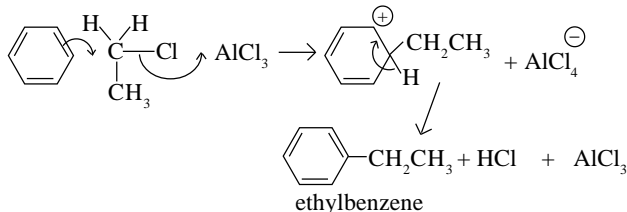

(c) Alkylation of benzene with chloroalkanes or acyl chlorides

Benzene reacts with chloroalkanes in the presence of anhydrous aluminium chloride to give an alkylbenzene.
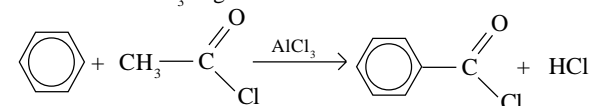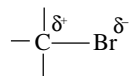

The mechanism is as follows:

A similar reaction mechanism occurs when benzene reacts with acid chlorides and $AlCl_3$ to give ketones.

5. Heterolytic Nucleophilic Substitution

Example: Halogenoalkanes with hydroxide ions and cyanide ions.

This mechanism is associated with polar covalent bonds (e.g. carbon-halogen).

$$-\overset{|}{\underset{|}{C}}\overset{\delta+}{}\!\!-\!\!\overset{\delta-}{Br}$$

The positive charge on the carbon allows attack by **nucleophiles** such as :OH⁻ or :CN⁻ which have lone pairs to donate.

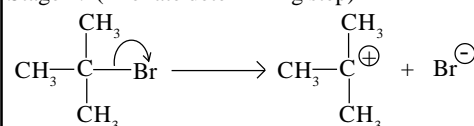There are two mechanisms for nucleophilic substitution, (1) S_N1 and (2) S_N2.
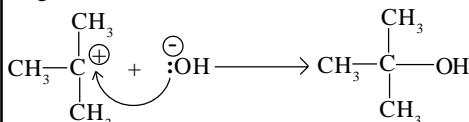
(1) S_N1 mechanism

This mechanism involves the substitution of a nucleophile which is first order (one molecule in rate determining step).

This mechanism occurs in two stages:

Stage 1: (The rate determining step)

Stage 2:

The first stage is rate determining as the second stage occurs much faster. Therefore the rate equation is:

$$\text{Rate} = k[(CH_3)_3CBr]$$

The reaction is zero order with respect to the nucleophile (OH⁻) as it does not take part in the rate determining step.

This mechanism involves the formation of an intermediate - the carbocation.

(2) S_N2 mechanism

The mechanism involves the substitution of a nucleophile which is second order (two molecules in rate determining step).

The nucleophile attacks the $C^{\delta+}$ and starts to form a covalent bond with it. At the same time the $C^{\delta+}$-Hal$^{\delta-}$ bond starts to **break** heterolytically.

This is one continuous process with the carbon-nucleophile bond getting stronger and the carbon-halogen getting weaker.

The "transition state" (corresponding to the activation energy peak) is when both are of equal strength.
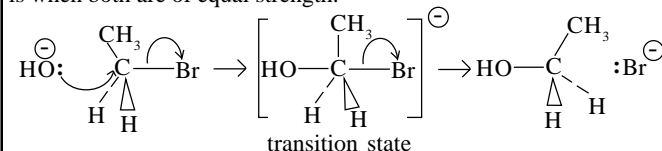
transition state

The formation of the transition state represents the rate determining step. This step is first order with respect to the halogenoalkane **and** the nucleophile.

$$\text{Rate} = k[CH_3CH_2Br][OH^{\ominus}]$$

S_N1 or S_N2?

To find out which mechanism is followed for such nucleophilic substitution reactions, the reaction rate must be followed by experiment and the rate order with respect to the nucleophile discovered.

In general the mechanism depends on the stability of the carbocation.

Alkyl groups are more "electron donating" than hydrogen atoms, so the carbocation of a tertiary group is more stable than that of a primary group.
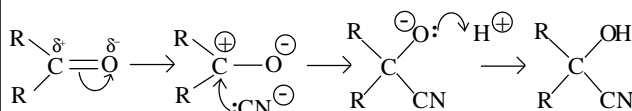

| Primary | Secondary | Tertiary |
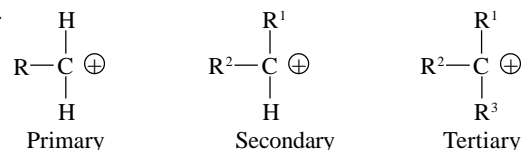
favour S_N2 ⟶ **favour S_N1**

6. Heterolytic Nucleophilic Addition

Example: Carbonyl compounds and hydrogen cyanide.

A nucleophile will attack the δ+ carbon in the C=O group.

Questions.

1. What is this difference between homolytic and heterolytic fission of bonds?

2. Show the reaction mechanisms for the following reactions:
   (a) $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$

   (b) $C_2H_5CHCH_2 + HBr \rightarrow C_2H_5CHBrCH_3$

   (c) $C_2H_5COCH_3 + HCN \rightarrow C_2H_5C(OH)CH_3CN$
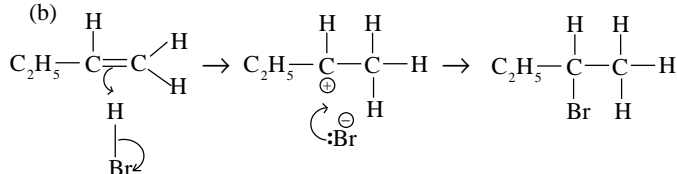
Answers

1. Homolytic fission is when a bond breaks with one electron going to each of the bonded atoms forming two free radical species. Heterolytic fission is when a bond breaks with both of the bond pair electrons going to one of the bonded atoms, forming a cation and anion.

2. (a) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

   (b)

   (c)