Edexcel IAL Chemistry A-level

Detailed notes
Topic 10A: General Principles

Classification of Reactions

Reactions can be classified according to what happens to the reactants during the reaction and the identity of the end products. The polarity of a bond will influence the types of reactions it may undergo. The main types of reactions are:

- **Addition** - In an addition reaction the reactants combine to form a single product.

- **Elimination** - In an elimination reaction a pair of atoms or two groups of atoms are removed from a molecule.

- **Substitution** - In a substitution reaction one functional group is replaced with a different functional group.

- **Oxidation** - A species loses at least one electron and is oxidised.

- **Reduction** - A species gains at least one electron and is reduced.

- **Hydrolysis** - A reaction in which a molecule is broken down by its reaction with water.

- **Polymerisation** - A reaction in which many small molecules known as monomers join together to form a long, repeating molecule called a polymer.

Mechanisms

Reaction mechanisms show the movement of electrons within a reaction. The movement of electrons is indicated by curly arrows. The mechanisms show how this movement of electrons results in the formation of products from reactants.

Bond breaking

Reactions involve the rearrangement of atoms and bonds and therefore require breaking and making bonds. There are two types of covalent bond breaking: homolytic and heterolytic.

In heterolytic fission one atom receives both electrons from the breaking of the covalent bond, while the other atom receives none. This bond-breaking forms ions: the atom that gains both of the electrons will form a negative ion and the other atom will form a positive ion. This, therefore, forms one electrophile (the positive ion) and one nucleophile (the negative ion).

**Electrophile**: A species that can accept electrons in a reaction, to form a chemical bond.

**Nucleophile**: A species that can donate electrons in a reaction, to form a chemical bond.
Topic 10B: Halogenoalkanes

Introduction to Halogenoalkanes
Halogenoalkanes contain polar bonds, since the halogens are more electronegative than a carbon atom. This means electron density is drawn towards the halogen, forming $\delta^+$ and $\delta^-$ regions.

Example:

![Halogenoalkane structure](image)

Halogenoalkanes can be classed as primary, secondary or tertiary halogenoalkanes depending on the position of the halogen within the carbon chain.

### Relative Reactivity
Reactivity varies depending on the halogen present in the molecule. Electronegativity of the halogens decreases down the group, meaning that a carbon-fluorine bond is much more polar than a carbon-iodine bond. Along with the fact that the carbon-fluorine bond is shorter, this means that the carbon-fluorine bond is much stronger than the carbon-iodine bond.

The greater the Mr of the halogen in the polar bond, the lower the bond enthalpy. A lower bond enthalpy means the bond can be broken more easily. Therefore, the rate of reaction increases for halogenoalkanes as you move down the group.

### Nomenclature
Halogenoalkanes are named using halogen prefixes and alkane stems.

#### Prefixes:

<table>
<thead>
<tr>
<th>Halogen functional group</th>
<th>Prefix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine</td>
<td>Fluoro-</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Chloro-</td>
</tr>
<tr>
<td>Bromine</td>
<td>Bromo-</td>
</tr>
<tr>
<td>Iodine</td>
<td>Iodo-</td>
</tr>
</tbody>
</table>
Stem:

<table>
<thead>
<tr>
<th>Number of C atoms</th>
<th>Prefix</th>
<th>Alkane example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Meth-</td>
<td>Methane</td>
</tr>
<tr>
<td>2</td>
<td>Eth-</td>
<td>Ethane</td>
</tr>
<tr>
<td>3</td>
<td>Prop-</td>
<td>Propane</td>
</tr>
<tr>
<td>4</td>
<td>But-</td>
<td>Butane</td>
</tr>
<tr>
<td>5</td>
<td>Pent-</td>
<td>Pentane</td>
</tr>
<tr>
<td>6</td>
<td>Hex-</td>
<td>Hexane</td>
</tr>
<tr>
<td>7</td>
<td>Hept-</td>
<td>Heptane</td>
</tr>
<tr>
<td>8</td>
<td>Oct-</td>
<td>Octane</td>
</tr>
<tr>
<td>9</td>
<td>Non-</td>
<td>Nonane</td>
</tr>
<tr>
<td>10</td>
<td>Dec-</td>
<td>Decane</td>
</tr>
</tbody>
</table>

If more than one particular side chain or functional group is present then one of the following prefixes is added: **di-** (2), **tri-** (3), **tetra-** (4), etc. If multiple prefixes are present, they are included in **alphabetical order**.

Example: The skeletal structure of 1,2-dichloropropane

![Skeletal structure of 1,2-dichloropropane](https://bit.ly/pmt-cc)

Reactions of Halogenoalkanes

**To produce Alcohols**
Halogenoalkanes can react with **aqueous alkali**, such as aqueous sodium or potassium hydroxide, to produce **alcohols** in a **nucleophilic substitution** reaction. The **hydroxide ion** acts as a **nucleophile**.

**To produce Alkenes**
Halogenoalkanes can react with **ethanolic potassium hydroxide** (KOH) to produce **alkenes** in an **elimination** reaction. The **hydroxide ion** acts as a **base**.

**Hydrolysis with Silver Nitrate**
Halogenoalkanes can be broken down in their reaction with aqueous silver nitrate and ethanol. The water in the solution acts as a nucleophile which leads to the breaking down of the halogenoalkane, releasing the halide ions into the solution. The halide ions then react with the silver ions from silver nitrate to form silver precipitates.

The colour of the precipitate allows you to identify the halide ion present. The rate at which the precipitates forms allows you to identify the relative stability of the halogenoalkanes, because the faster the precipitate forms, the less stable the halogenoalkane, and therefore the more quickly it is hydrolysed.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>Br⁻</td>
<td>I⁻</td>
</tr>
<tr>
<td>White precipitate (AgCl)</td>
<td>Cream precipitate (AgBr)</td>
<td>Yellow Precipitate (AgI)</td>
</tr>
</tbody>
</table>

Reactivity depends on the strength of the C-X bond (where X is a halogen atom) and not the bond polarity. Bond strength decreases with increasing Mr. Therefore, iodoalkanes would react faster than bromoalkanes and chloroalkanes, and bromoalkanes would react faster than chloroalkanes.

To produce Amines
Halogenoalkanes can react with alcoholic ammonia (for example, with ethanolic NH₃) to form amines in a nucleophilic substitution reaction. Ammonia acts as a nucleophile.

To produce Nitriles
Halogenoalkanes can react with alcoholic potassium cyanide (KCN) to form nitriles in a nucleophilic substitution reaction. The cyanide ion, CN⁻, acts as a nucleophile. This reaction adds on a carbon atom, so it can be used in synthesis routes to increase the length of carbon chains.

Nucleophilic Substitution

Nucleophiles
These species are ‘positive liking’. They contain a lone electron pair that is attracted to \(\Delta^+\) regions of molecules. Some of the most common nucleophiles are:

- CN⁻
- `NH₃`
- `OH`

They must be shown with the lone electron pair to make it clear that they are nucleophiles.
Nucleophilic Substitution

Nucleophilic substitution is the reaction mechanism that shows how nucleophiles attack halogenoalkanes. From halogenoalkanes, aqueous potassium hydroxide is used to produce alcohols, potassium cyanide is used to produce nitriles and ammonia is used to produce amines.

**Mechanism: Alcohol**

The nucleophile attacks the $\delta^+$ carbon and the electrons are transferred to the chlorine.

**Mechanism: Amines**

The intermediate has a positively charged nitrogen ($N^+$). Electrons are transferred to the nitrogen by the loss of a hydrogen atom.

Nucleophilic substitution reactions can only occur for primary and secondary alkanes.

### 10C: Alcohols

**Introduction to Alcohols**

Alcohols contain an -OH group and follow the general formula $C_nH_{2n+1}OH$. They can be produced via two main methods of fermentation or hydration. Alcohols are named according to IUPAC rules and have the suffix -ol. Alcohols can be primary ($1^\circ$), secondary ($2^\circ$) or tertiary ($3^\circ$) depending on the position of the hydroxyl group.
Example: Benzene-1,3-diol

Reactions of Alcohols

Combustion
When burned in air, alcohols react with oxygen to form carbon dioxide and water. Alcohols make good fuels by reacting in this way as lots of energy is also released.

$$2\text{CH}_3\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$$

Reactions with Halogenating Agents
Alcohols can react with halogenating agents via nucleophilic substitution. The -OH group is replaced by a halogen, producing a halogenoalkane.

PCl₅ is used to produce chloroalkanes. This can be used as a test for alcohols because their reaction with PCl₅ produces white steamy fumes that turn damp blue litmus paper red.

A reaction mixture of 50% concentrated sulfuric acid and potassium bromide can be used to produce bromoalkanes. The potassium bromide reacts with the sulfuric acid to form HBr. This then reacts with the alcohol to produce the bromoalkane.

$$\text{CH}_3\text{CH}_2\text{OH} + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$$
A reaction mixture of **red phosphorus** with iodine can be used to produce **iodoalkanes**. First the phosphorus reacts with the iodine to produce **phosphorus(III) iodide**. This then reacts with the alcohol to form the iodoalkane.

\[
2P + 3I_2 \rightarrow 2PI_3 \\
3CH_3CH_2OH + PI_3 \rightarrow 3CH_3CH_2I + H_3PO_3
\]

**Elimination Reactions**
Alkenes can be formed from the **dehydration of alcohols**, where a molecule of water is removed from the molecule. In order to do this, **concentrated phosphoric acid** is added as a reagent.

**Oxidation of Alcohols**

Primary and secondary alcohols can be **oxidised** to produce various products but tertiary alcohols are **not easily oxidised**.

When primary alcohols are heated in the presence of **acidified potassium dichromate(VI)**, they are **oxidised** to aldehydes. **Distillation** is required to separate the aldehyde product.

**Example:**

![Ethanol to Ethanal conversion](image)

When heated further under **reflux** conditions, primary alcohols are **oxidised further** to **carboxylic acids**.

**Example:**

![Ethanal to Ethanoic Acid conversion](image)
Secondary alcohols can be oxidised when heated in the presence of acidified potassium dichromate(VI) to produce ketones.

**Example:**

![Chemical reaction](image)

**Potassium Dichromate(VI) (K₂Cr₂O₇)**

Potassium dichromate(VI) is used in the oxidation of alcohols as the oxidising agent. It is reduced as the alcohol is oxidised. A colour change from orange to green is observed when the alcohol is oxidised with potassium dichromate(VI).

![Colour change](image)

**Test for Aldehydes**

Aldehydes are tested for using Tollens’s reagent or Fehling’s solution.

A few drops of Fehling’s solution are added and the test tube is gently warmed. If an aldehyde is present a red precipitate will form. If no aldehyde is present the solution will remain blue.

Aldehydes can be identified in the same way using Tollens’s reagent. If an aldehyde is present a layer of silver will form on the walls of the test tube. If no aldehyde is present the solution will remain colourless.
Ketones will not give a positive result with either of these tests.

**Test for Carboxylic Acids**
Carboxylic acids react with metal carbonates to form a salt and carbon dioxide gas. **Sodium carbonate** or **sodium hydrogencarbonate** can be used to identify the presence of a carboxylic acid from the complete oxidation of primary alcohols. A salt will form and the solution will effervesce as a gas is released. If this carbon dioxide gas is bubbled through **limewater** it will cause the limewater to turn cloudy due to the formation of a white precipitate.

**Experimental Techniques**

There are many different techniques that can be used to prepare and then purify an organic compound.

**Heating under Reflux**
Reflux apparatus is used to continually heat the contents of the flask to allow reactions like the oxidation of primary alcohols to proceed all the way to the formation of carboxylic acids. The **condenser** helps ensure the vapours condense and return to the flask for further heating. This ensures the product vapours can not escape.
Separating Funnel
A separating funnel is used to separate two liquids with different densities. The mixture is added to the flask and the liquids are allowed to separate into two layers. The tap can then be opened to collect the bottom, denser liquid in one flask and the second, less dense liquid in a second flask.

Distillation
Distillation apparatus is used to separate liquids with different boiling points. The pear-shaped flask is heated and the liquid with the lower boiling point will evaporate first. It rises out of the flask and into the attached tubing which is surrounded by a condenser. The condenser causes the vapour to cool and condense back into a liquid, which is then collected in a separate flask.

Drying
A compound can be dried by the addition of an anhydrous (contains no water) salt. The anhydrous salt will absorb moisture and water present, thus drying and purifying the compound. A common anhydrous salt used for drying is sodium sulphate.

Boiling point determination
Determining the boiling point of a compound and comparing it to a databook value is a way of testing its purity. The purer a substance, the closer to the databook boiling point value it will be. If a sample has a low purity, the melting or boiling point will take place over a range of temperatures.
To determine the boiling point, the substance is packed into a **Thiele tube** which has an **inverted capillary tube** in it. The substance is heated to above its boiling point and allowed to cool. When it **condenses** into a liquid it will be drawn into the capillary tube and the temperature at which this change occurs is taken to be the boiling point.

### 10D: Mass spectra and IR

**Mass Spectrometry**

Mass spectrometry is an **analytical technique** used to identify different isotopes and to find the overall **relative atomic mass** of an element. Further details of the process can be found in **Topic 2**.

During the ionisation process, a **2+ charged ion** may be produced. Its mass to charge ratio (m/z) is halved - this can be seen on spectra as a trace at **half the expected m/z value**.

**Example:**


Using this spectrum, the **Ar can be calculated**:

**Example:**

\[
\text{Ar} = \frac{\text{m}/\text{z} \times \text{abundance}}{\text{Total abundance}} = \frac{(10 \times 75) + (12 \times 25)}{75 + 25} = 10.5
\]

**Infrared (IR) Spectrometry**

Infrared spectroscopy is an analytical technique which uses **infrared (IR) radiation** to determine the **functional groups** present in organic compounds. The IR radiation is passed through a sample where the different types of bonds **absorb** the radiation in different amounts. These varying amounts of absorbance are **measured and recorded**, allowing certain bonds, and thus functional groups, to be identified.
A spectrum is produced from the measurements, which has characteristic curves for the different functional groups:

**-OH Alcohol Group**

The characteristic -OH alcohol group peak is in the range $3230 - 3550 \text{ cm}^{-1}$.

**-OH Acid Group**

The characteristic -OH acid group peak is in the range $2500 - 3300 \text{ cm}^{-1}$.
C=C Unsaturated Group

The characteristic C=C peak is in the range 1620 - 1680 cm\(^{-1}\).

C=O Carbonyl Group

The characteristic C=O peak is in the range 1680 - 1750 cm\(^{-1}\).

Fingerprint Region

Each IR spectrum has a fingerprint region to the right-hand side, from 500-1500 cm\(^{-1}\). This is unique for each species, containing tiny differences between each species. This means it acts as a molecules’ ‘fingerprint’, allowing it to be identified.