Higher Chemistry

\[ \text{H} \]
\[ \text{C—C—C—C = O} \]

Unit 2:

Nature's Chemistry

Pupil Notes

Part 3

Oxidation

Reactions
5.3 Oxidation Reactions

This topic examines how the different types of alcohol are oxidised and the different types of product produced.

Comparing Oxidation

This activity compares the oxidation reactions of the three types of alcohol.

<table>
<thead>
<tr>
<th>Name of alcohol</th>
<th>Type of alcohol</th>
<th>Colour change observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>butan-1-ol</td>
<td>primary</td>
<td></td>
</tr>
<tr>
<td>butan-2-ol</td>
<td>secondary</td>
<td></td>
</tr>
<tr>
<td>2-methylpropan-2-ol</td>
<td>tertiary</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aci potassium dichr</th>
<th>a mild oxidising agent that changes col when it reacts.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} )</td>
<td>orange green</td>
</tr>
</tbody>
</table>

A large number of \( \text{H}^+ \) ions are consumed, hence the need to use an \( \text{aci} \) solution or reaction would be too \( \text{sl} \).

Three different types of alcohol were added to some \( \text{dichromate} \) solution and placed in a hot \( \text{wa} \) bath for a few minutes.

Both Prim and Sec alcohols can be oxidised but Tertiary alcohols cannot.

The Oxidation Reaction

This activity explains the changes which occur when different types of alcohol are oxidised.

Prim alcohols can be oxi in two stages. The oxidising agent is simply the source of oxy \([O]\).

During the first stage the \( \text{hyd} \) group \( \text{C}—\text{OH} \) is converted into a \( \text{carb} \) group, \( \text{C}=\text{O} \). The molecule produced is called an \( \text{ald} \).
The second stage sees the **aldehyde** converted into an **acid**.

\[
\begin{array}{c}
\text{R-} \text{C} = \text{O} \\
\text{H} \\
\text{[O]}
\end{array} \rightarrow \begin{array}{c}
\text{R-} \text{C} = \text{O} \\
\text{O-} \text{H}
\end{array}
\]

Notice that **oxi** can involve the **loss of hyd** as well as the **gain of ox** (and, of course, oxidation is still the **loss of elec**).

In Organic Chemistry it is often more convenient to use the following definitions:

**OXIDATION** - an *increase* in the oxygen:hydrogen ratio (O or H)

**REDUCTION** - a *decrease* in the oxygen:hydrogen ratio (O or H)

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular Formula</th>
<th>Number of O atoms</th>
<th>Number of H atoms</th>
<th>Oxygen: Hydrogen ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>C₂H₆O</td>
<td>1</td>
<td>6</td>
<td>1:6</td>
</tr>
<tr>
<td>ethanal</td>
<td>C₂H₄O</td>
<td>1</td>
<td>4</td>
<td>1:4</td>
</tr>
<tr>
<td>ethanoic acid</td>
<td>C₂H₄O₂</td>
<td>2</td>
<td>2</td>
<td>1:2</td>
</tr>
</tbody>
</table>

**Sec** **alcohols** can also be **oxi**, but they can only go through the first stage. Again, the oxidising agent is simply the source of **oxy** \([\text{O}]\).

\[
\begin{array}{c}
\text{R-} \text{C} \text{O} \text{H} \\
\text{R} \text{R} \text{[O]}
\end{array} \rightarrow \begin{array}{c}
\text{R-} \text{C} = \text{O} \\
\text{R-} \text{H} \\
\text{H₂O}
\end{array}
\]

Again, during the first stage of oxidation the **hyd** group \(\text{C—OH}\) is converted into a **carb** group, \(\text{C}=\text{O}\). The molecule produced this time is called a **ket**. The absence of a **hyd** atom makes it impossible for this molecule to be **oxi** a second time to form an **ac**.

**Ter** **alcohols** cannot be **oxi**. The absence of **hyd** atoms makes **oxidation** impossible.
This activity investigates another method for oxidising primary and secondary alcohols.

When a primary alcohol is passed over heated copper (II) oxide the oxide turns into red-brown copper metal.

A piece of pH paper held at the mouth of the test-tube turns red — an acid has been formed.

When a secondary alcohol is passed over heated copper (II) oxide the oxide turns into red-brown copper metal.

A piece of pH paper held at the mouth of the test-tube stays the same because an acid has not been formed.

Summary

- A primary alkanol (—OH at end of chain)
  - butan-1-ol

- An alkanal (C=O at end of chain)
  - butanal

- An alkanoic acid (COOH at end of chain)
  - butanoic acid

- A secondary alkanol (—OH in middle of chain)
  - butan-2-ol

- An alkanone (C=O in middle of chain)
  - butanone

- A tertiary alkanol (—OH at same place as a branch)
  - 2-methylpropan-2-ol
**Oxidation of Aldehydes**

This activity investigates other oxidising agents that can be used to distinguish aldehydes from ketones.

Acidified potassium dichromate is a mild oxidising agent that changes color when it reacts.

\[ \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \]

Orange            green

A large number of ions are consumed, hence the need to use an acidified solution or reaction would be too slow.

Fehling’s or Benedict's are another two mild oxidising agents that change color when they react.

\[ \text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+ \]

Blue        red-brown

Solution          solid

Tollen’s solution is another mild oxidising agent that changes state when it reacts.

\[ \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag} \]

Colourless       silvery

Solution          solid

Sometimes the silver attaches to the surface to give a 'silver mirror' effect.

Tollen’s and Fehling’s solutions can only be used to oxidise aldehydes. They do not usually react with primary or secondary alcohols. This makes acidified dichromate the only 'universal' oxidising agent.

**Food Chemistry 1**

The aim of this activity is to introduce some of the oxygen containing compounds that have important roles as flavour molecules and the problems that oxidation can bring.

Though there are many molecules responsible for the valued smell of truffles, two alcohols and two aldehydes are found in the highest concentration. Alcohols and aldehydes such as these are easily oxidised. When that happens, the truffles lose their characteristic aroma and flavour.

\[
\begin{align*}
\text{2-methylbutanol} & \quad \text{3-methylbutanol} \\
& \quad \text{2-methylbutanal} \quad \text{3-methylbutanal}
\end{align*}
\]
Most flavour molecules are more complex, but many contain the **alc**, **ald** or **ket** functional groups. They can be, however, vulnerable to **oxi** which will almost certainly change the nature of their **fla**. While small acids such as **meth** and **eth** acid are ‘vinegary’, others such as **prop** and **but** acid are ‘cheesey’ and ‘sickly’ and can be responsible for the **rancid** smells of food ‘going off’.

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**Benzaldehyde — almond**

**Vanillin — vanilla beans**

**Cinnamaldehyde — cinnamon**

**Citral — lemongrass**

**2-Octanone — mushroom flavoring**

No **oxidation** product as this only contains the **ketone** group.
Free Radicals  
The aim of this activity is to introduce free radicals.

Organic chemistry largely involves stable molecules with covalent bonds - a pair of electrons shared between two atoms.

Often, reactions involve the breaking of bonds to form temporary, very reactive ions (the activated complex) and electrons tend to remain as a pair of electrons. Ions with 4 pairs of electrons - the stable octet - will not need to react further.

There are many reagents that can react with the metal ion produced.

One of these is the hydroxide ion which will quickly react to form an alcohol.

Overall the reaction would be:

$$\text{CH}_3\text{Cl} + \text{NaOH} \rightarrow \text{CH}_3\text{OH} + \text{NaCl}$$

Since both products are stable this reaction will effectively be over and, as is often the case, the products will be more stable than the reactants and, overall, energy will have been released to the surroundings.
Whilst *po bo* are generally easier to break, *n-po bo* can also break, though extra *en*, in the form of *li*, is often required. When these bonds *br*, each atom retains its own electron but *very uns*, *very rea* free radicals are formed.

When *li* of the correct *en* strikes a *bo*, the *en* can be ab.

\[
\text{Cl} - \text{Cl} \rightarrow 2 \text{Cl}^* 
\]

In *chl* mol, Cl₂, each *chl* at is surrounded by 4 *ele pa* and they are *st*. When the bond *bre*, each *chl* atom has only 3 *ele pa*. There are still *eq num s* of *ele* and *ele* present so these are *at not io*.

Similarly, the *n-po O — O bo* in *hy pero* can easily break to produce *fr rad*:-

\[
\text{H} - \text{O} - \text{O} - \text{H} \rightarrow \text{H} : \text{O}^* - \text{O} : \text{H} 
\]

**Free Radical Chain Reaction**

The aim of this activity is to examine how reactions involving free radicals lead to a chain reaction.

When a *fr rad* reacts with another *mol*, a new *fr rad* is always produced. This new *fr rad* can then go on and react to *pro ano free radical* and so the *rea con* ‘forever’ - a *ch rea*.

For example, the *sub* reaction between and *alk* and a *hal* has a number of steps which will repeat ‘forever’.

**Initiation:** needed to produce a free radical to start each chain.

\[
:\text{Cl} : \text{Cl} : + \text{photon} (hv) \rightarrow + 
\]

**Propagation:** the steps that will see a free radical react but a new free radical produced to keep the chain reaction going.

\[
\text{H—C—H} + \text{Cl}^* \rightarrow + 
\]

methane chlorine atom methyl radical hydrogen chloride
Second propagation step

Termination: the steps that will see a chain eventually stopped

Detailed descriptions of the steps involved in a reaction - showing the movement of electrons as bonds break and form - is called a Reaction Mechanism.

Overall the reaction is simply:

$$\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$$

This is another example of a Substitution reaction and is the characteristic reaction of saturated hydrocarbons such as alkane. The reaction with bromine vapour or bromine water is often used as the test for saturation. Both saturated and unsaturated molecules can decolourise bromine, but at very different rates,

$$\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr} \quad \text{sl, sub, in light}$$

$$\text{C}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_4\text{Br}_2 \quad \text{fa, add, even in dark}$$
Free Radical Oxidation

The aim of this activity is to examine how free radical oxidation leads to problems with food shelf-life as well as natural ageing in organisms.

The radicals of most concern in biological systems are derived from ox and are known collectively as reactive oxygen species or RAS. The main 3 are opposite:

- superoxide \( \cdot \cdot \cdot \cdot O \)
- peroxide \( \cdot \cdot \cdot \cdot O^2 \)
- hydroxyl \( \cdot \cdot \cdot \cdot H \)

Whilst some radicals are formed by external processes, many are formed as necessary intermediates in a variety of normal biochemical reactions.

However, when generated in excess or not appropriately controlled (by natural antioxidants), radicals can wreak havoc on a broad range of molecules, such as lipids (fats & oils), phospholipids (cell membranes) and proteins including parts of DNA and RNA.
Macromolecules such as lip (derived from fatty acids), pro and nuc acids (DNA) are particularly vulnerable to damage through a process known as lipid peroxidation.

The reaction between ox based rad and the C = C dou bond can often progress from:

- $\text{—OH}$ hyd
- $\text{—C = O}$ carb
- $\text{—COOH}$ carb

and the carbon ch will often br at the site of the original C = C bond.

**Antioxidants**

The aim of this activity is to examine some antioxidants and the types of food in which they can be found.

If fats oxi, they can produce “off” od and fla (stale, rancid odours). Many of the molecules produced are ald, ket or carb acids.

Many vit also oxidise and lose their activity.

If food pigm oxidise, they can change col completely. For example, red meat turns gray when the myoglobin pigm oxi. In this case, the product is not unsafe; it just looks less appealing.

Antioxidants can be classified as one of two types:

- ‘traditional’ red agents or free rad scav
- Sulph (SO$_2$ $\rightarrow$ SO$_3^-$ in water) to slow down or prevent oxidation. Sausages and other processed meats similarly use sulph or nitr as pres.

Similarly, Vit C (ascorbic acid) is a natural anti found in many foods.
Many of our *anti* *oxi* agents are also *free* *rad* scavengers which can react with free radicals but form stable molecules and prevent chain reactions.

By moving the single electron around the molecule, it is possible to form a stable radical and stop the chain reaction. In addition, this molecule can go on and 'mop up' a second radical making them even more effective.

**Free Radical Scavengers**

The aim of this activity is to examine some other applications of Free Radical Scavengers.

It is not just food that we need to protect from *oxi* brought about by exposure to *UV* present in *sun* .

**Sun Blocks:** whilst they contain white *pigments*, such as titanium oxide, which try and block the *UV light*, they also contain *free* *rad* scavengers to help minimise the damage caused by *free radicals* - such as *aging*.

**Cosmetics:** for similar reasons, many *cosmetics* now include *free* *rad* scavengers among their *ingredients*.

**Plastics:** many *plastics* contain groups that are vulnerable to *free* *oxi* radicals so *free* *rad* scavengers are added to prolong their use.

However, other plastics deliberately incorporate *UV* *absorbers* groups to accelerate the breakdown of the *plastics* and make it more *biodegradable*. 