Higher Chemistry

Topic 5:

Organic 1

Study Guide 3

Oxidation Reactions
Oxidation Reactions 5.3

Introduction

The combustion reactions of organic molecules are examples of oxidation since the molecules react with oxygen from the air. Such oxidation is quite severe since the entire molecule is broken up in the process to form carbon dioxide and water.

This topic is about a milder oxidation reactions which only affect the functional group and leave the carbon chain of the alcohol intact. Oxidising agents can include ions that are readily reduced as well as Free Radicals - atoms or molecules with an unpaired electron. 

This lesson topic explores the effect of oxidation on organic molecules.

Oxidation of Alcohols

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

Primary, secondary and tertiary alcohols react differently with mild oxidising agents such as acidified dichromate solution. As the alcohol is oxidised by the dichromate ion a colour change takes place in the solution.

What to do

1. Collect a beaker of hot water and keep it at your work place.
2. Pour a 1 cm depth of acidified dichromate solution into three test-tubes.
3. To one test-tube add 5 drops of butan-1-ol, to the next add butan-2-ol, and to the third add 2-methylpropan-2-ol.
   
   Ensure the test-tubes are labelled to avoid mixing them up (e.g. with a piece of scrap paper in the mouth of each tube).
4. Place all three tubes in the beaker of hot water and observe any colour change after 5 minutes.

(Copy the table for recording your observations while you are waiting.)

<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></td>
<td></td>
</tr>
<tr>
<td>butan-2-ol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylpropan-2-ol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Complete the table using the results of your experiment.

Think about the results of your experiment.

- Which two alcohols caused a greenish colour to be produced?
- Were these alcohols primary, secondary, or tertiary?
- Which type of alcohol was not oxidised by acidified dichromate?
This activity explains the changes which occur when different types of alcohol are oxidised.

Primary alcohols can be oxidised in two stages. The first stage oxidises the alcohol to a compound known as an aldehyde.

To simplify the structures, only the carbon on the functional group is shown and the rest of the molecule is represented by \( R \).

The oxidising agent, acidified potassium dichromate, can be shown simply as a source of oxygen \([O]\).

In the second stage of oxidation, the aldehyde can be further oxidised to form an acid.

Think about the two stages of oxidation shown above.

- In the first stage, the alcohol does not actually gain any oxygen. What does happen to the alcohol molecule as it is oxidised in this reaction?
- What happens to the oxidising oxygen atom in the second stage?

The first stage of oxidation involves the alcohol molecule losing hydrogen atoms, whereas the second stage involves the aldehyde molecule gaining oxygen. The loss of hydrogen or the gain of oxygen are two ways of considering the process of oxidation.

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

**OXIDATION** - an increase in the oxygen:hydrogen ratio (gain oxygen or lose hydrogen)

**REDUCTION** - a decrease in the oxygen:hydrogen ratio (lose oxygen or gain hydrogen)

What to do

1. Draw full structural and molecular formulae for:
   - ethanol
   - ethanal
   - ethanoic acid

2. Work out the oxygen:hydrogen ratio for each molecule.

Think about the molecules you have drawn.

- What is the change in functional group during the first stage of oxidation? What happens to the oxygen:hydrogen ratio?
- What is the change in functional group during the second stage of oxidation? What happens to the oxygen:hydrogen ratio?

Secondary alcohols can only undergo one stage of oxidation to form compounds known as ketones.

All of the oxidation products from primary and secondary alcohols contain the C = O group in their molecules. This group of atoms is known as the carbonyl group.
**Tertiary alcohols** cannot undergo mild oxidation at all. The reason has to do with the structure at the \textit{hydroxyl} position.

Consider the tertiary alcohol in comparison with the other two.

- What does the tertiary structure not have that the other two do have?
- Why is it not possible for oxidation by removal of hydrogen atoms to occur with a tertiary alcohol?

\textbf{This activity investigates another method for oxidising primary and secondary alcohols.}

1. Push a small piece of ceramic wool to the bottom of a test-tube and add 10 drops of butan-1-ol.
2. Push a second piece of ceramic wool half way down the tube and sprinkle a little copper(II) oxide on to it.
3. Push a third piece of ceramic wool on top to hold the copper(II) oxide in place.
4. Set up the apparatus as shown and check that the wet pH paper is showing the neutral colour.
5. Heat the copper(II) oxide strongly for a three minutes. Enough heat should reach the alcohol without moving the bunsen thus causing alcohol vapour to pass along the tube and through the hot copper(II) oxide.
6. Observe what happens to the copper(II) oxide and the wet pH paper.
7. Clean out the test-tube and repeat the experiment using butan-2-ol.

During this reaction the copper(II) ions are being \textit{reduced} to copper atoms.

8. Write the ion-electron equation for this \textit{reduction}.

Think about the results of your two experiments.

- How could you tell that the copper(II) oxide had reacted? Did it react with both alcohols?
- How do the results of the experiment confirm that only the primary alcohol is oxidised to an acid?
- What was the secondary alcohol oxidised to?

Think about the equation you wrote.

- How can you tell that the copper II) oxide is being reduced?
**Self Check**

**Q1.** What colour change happens when acidified dichromate oxidises an alcohol?
   A blue to orange.
   B orange to green.
   C green to orange.
   D orange to purple.

**Q2.** Which of the following is not oxidised by acidified dichromate solution?

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td><img src="image1.png" alt="Structure A" /></td>
<td><img src="image2.png" alt="Structure B" /></td>
</tr>
</tbody>
</table>

**Q3.** Which type of alcohol can be oxidised in two stages?
   A primary alcohols only.
   B secondary alcohols only
   C primary and secondary alcohols only.
   D secondary and tertiary alcohols only.

**Q4.** Oxidation with acidified dichromate causes an alcohol molecule to
   A gain an oxygen atom.
   B gain hydrogen atoms.
   C lose an oxygen atom.
   D lose hydrogen atoms.

**Q5.** Mild oxidation of a secondary alcohol can produce
   A an acid.
   B a ketone.
   C an alkene.
   D an aldehyde.

**Questions 6, 7 and 8 refer to the following structural formulae.**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td><img src="image3.png" alt="Structure A" /></td>
<td><img src="image4.png" alt="Structure B" /></td>
<td><img src="image5.png" alt="Structure C" /></td>
<td><img src="image6.png" alt="Structure D" /></td>
</tr>
</tbody>
</table>

**Q6.** Which structure is formed by the mild oxidation of the following molecule?

**Q7.** Which molecule has the highest oxygen:hydrogen ratio?

**Q8.** In which structure is the carbonyl group not present?

**Q9.** When a primary alcohol reacts with hot copper(II) oxide
   A an alkali and copper are formed.
   B a ketone and copper are formed.
   C carbon dioxide and water are formed.
   D an acid and copper are formed.

**Q10.** When a secondary alcohol reacts with hot copper(II) oxide
   A an alkali and copper are formed.
   B a ketone and copper are formed.
   C carbon dioxide and water are formed.
   D an acid and copper are formed.
Oxidation of Aldehydes & Ketones

As you already know, it is possible to insert an oxygen into the aldehyde functional group but not a ketone. Only aldehydes can react with mild oxidising agents.

The aim of this activity is to plan an experiment that uses mild oxidising agents to distinguish between two carbonyl compounds: one an aldehyde and the other a ketone.

The oxidising agents to be used are (i) acidified dichromate solution, (ii) Fehling’s solution, and (iii) Tollen’s solution.

This can be used as another opportunity to fulfill some of the requirements of the Researching Chemistry Unit assessment. Your teacher will inform you if this is to be formally assessed.

Outcome 2

The candidate will:

2. Apply skills of scientific inquiry to investigate, through experimentation, the underlying chemistry of a chosen topic by:

2.1 Planning/designing the practical investigation, including safety measures.
2.2 Carrying out the practical investigation safely, recording detailed observations/measurements correctly

What to do

1. You will need to plan which aldehyde and which ketone you will use.
2. You will need to research any safety implications associated with these chemicals and the oxidising agents you will be using.
3. Your plan should include a clear aim for the practical investigation.
4. Your plan should include a clear and detailed description of how the practical investigation should be carried out including safety considerations. The plan may include labelled diagrams. Include any observations/measurements you intend to make.

Remember that there must be evidence that each member of the group contributed to the planning of the practical investigation.

5. You will be observed to ensure that you follow procedures safely.
6. Observations/measurements should be recorded correctly and results presented in an appropriate format. All raw data must be recorded.
7. Each member of the group must have a complete record of their work.

Remember that there must be evidence that each member of the group contributed to the carrying out of the practical investigation.

Consider the investigation you have just carried out.

- Have you done enough to satisfy the requirements of Outcome 2?
- Can these oxidising agents be used to distinguish between an aldehyde and a ketone?
Questions 1 to 3 refer to the following structural formulae.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H} \text{O} ) ( \text{H-C-C-O-H} ) ( \text{H} )</td>
<td>( \text{H} \text{O} ) ( \text{H-C-C-C-H} ) ( \text{H} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H} \text{O} ) ( \text{H-C-C-C-H} ) ( \text{H} )</td>
<td>( \text{H} \text{O} ) ( \text{H-C-C-O-H} ) ( \text{H} )</td>
</tr>
</tbody>
</table>

**Q1.** Which molecule is an alkanal?

**Q2.** Which molecule is an alkanone?

**Q3.** Which molecule has the highest oxygen:hydrogen ratio?

**Q4.** The correct systematic name for the following molecule is

\[
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CHO}
\]

A 2-methylbutanal.
B 2-methylbutanone.
C 3-methylbutanal.
D 3-methylbutanone.

**Q5.** The correct systematic name for the following molecule is

\[
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{COCH}_3
\]

A pentan-2-al.
B pentan-2-one.
C pentan-4-al.
D pentan-4-one.

**Q6.** Which of the following can be used to distinguish an aldehyde from a ketone?

A moist pH paper
B bromine solution
C cobalt chloride paper
D fehling’s solution

**Q7.** In a positive test with Tollen’s solution the colour change is from

A colourless to dark brown or silver
B blue to orange or red
C colourless to orange or red
D blue to dark brown or silver.

**Q8.** In a positive test with Fehling’s solution the colour change is from

A colourless to dark brown or silver
B blue to orange or red
C colourless to orange or red
D blue to dark brown or silver.

**Q9.** Which from the following molecules will give a negative test with Tollen’s solution?

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O} ) ( \text{H-C-H} )</td>
<td>( \text{H} \text{O} ) ( \text{H-C-C-H} ) ( \text{H} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O} \text{O} ) ( \text{H-C-C-C-H} ) ( \text{H} )</td>
<td>( \text{H} \text{O} ) ( \text{H-C-C-C-H} ) ( \text{H} )</td>
</tr>
</tbody>
</table>

**Q10.** A ketone does not undergo mild oxidation because its carbonyl group

A has no hydrogen atom joined to it.
B is not part of a carbon chain.
C has no other oxygen atom available.
D is not the right way round.
Food Chemistry - Alcohols, Aldehydes, Ketones & Acids

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.

Truffles are one of the most highly prized ingredients in most of the finest kitchens in the world. In fact, the truffle has been described as the “diamond of the kitchen.”

Many have studied the compounds in truffles that produce the aroma, and hence the flavor. They have found as many as thirty-six components of that flavor profile, including alcohols, aldehydes, ketones, carboxylic acids, esters, amines, aromatic compounds, and hydrocarbons—virtually an entire organic chemistry laboratory!

Two alcohols and two aldehydes are found in the highest concentrations. These are 2-methylbutanol, 3-methylbutanol, 2-methylbutanal, and 3-methylbutanal. As you have learned in this lesson, alcohols and aldehydes such as these in the truffle flavor profile are easily oxidised.

When that happens, the truffle loses the molecules that are characteristic of its aroma and flavor. Fresh truffles must be used quickly and stored carefully to retain the flavor.

1. Draw the structures of the molecules that are responsible for the flavour of truffles.

2. Write equations for the oxidation reactions that destroy the complex aroma and flavor of truffles.

Alcohol abuse kills more than 75,000 americans a year. Ethanol consumed from alcoholic drinks is first oxidised into ethanal in the liver. Ethanal is much more toxic than ethanol and is responsible for many of the symptoms of a hangover.

Normally, an enzyme then converts the ethanal into ethanoic acid, which is then used in biochemical pathways that harvest energy for cellular work or that synthesise fats.

Antabuse inhibits the enzyme. This inhibition occurs within 1 to 2 hours of taking the drug and continues up to 14 days. When a person who has taken Antabuse drinks an alcoholic beverage, the level of ethanal quickly reaches levels that are five to ten times higher than would normally occur after a drink. Within just a few minutes, the symptoms of a severe hangover are experienced and may continue for several hours.

3. Write equations for the oxidation reactions described above.

Alcohol is widely used as a solvent for flavour molecules such as vanillin, that would struggle to dissolve in highly polar water. The alcohol is sufficiently less polar than water but often the addition of water will lead to the oil losing its solubility and it will form a cloudy suspension. This is often called the “ouzo effect”
Most flavour molecules are more complex, but many contain the alcohol, aldehyde or ketone functional groups.

They can be, however, vulnerable to oxidation which will almost certainly change the nature of their flavour.

While small acids such as methanoic and ethanoic acid are ‘vinegary’, others such as propanoic and butanoic acid are ‘cheesey’ and ‘sickly’ and can be responsible for the rancid smells of food ‘going off’

For each of the flavour molecules shown below, draw the molecule that would be produced if it was oxidised.
5.3c

**Self Check**

Q1. When wine “goes bad,” the ethanol is converted into

A  CH₃COOH  
B  CH₃OCH₃  
C  CH₃CH₂OH  
D  CH₃OH

Q2. In which of the following is the C=O group not found

A  an ester  
B  a carboxylic acid  
C  a ketone  
D  an amine

Q3. Which of the following conversions does not involve oxidation?

A  propan-1-ol to propanal  
B  propene to propan-2-ol  
C  propan-2-ol to propanone  
D  propanal to propanoic acid

Q4. The shortened structural formulae for two compounds are given below:

CH₃CH₂CH₂CH=CHCHO  
CH₃CH₂CH(CH₃)COCH₂CH₃

Which characteristic applies to both compounds?

A  both decolourise bromine water  
B  both are branched molecules  
C  both can be made by the oxidation of alcohols  
D  both are saturated molecules

Q5. How many isomers with molecular formula C₄H₈O can react with Fehling’s solution?

A  1  
B  2  
C  3  
D  4

Q6. Female German cockroaches convert the alkane shown below to a substance that attracts males.

CH₃CH₂CH(CH₂)₇CH(CH₂)₆CH₂CH₃

Oxidation at the C-2 of the alkane gives the sex attractant which has a molecular formula of C₂₁H₴₂O. Which of the following is the sex attractant?

A  OH  
B  OH  
C  CO  
D  O

Q7. Which one of the following conversions does not represent a reduction?

A  propene → propan-2-ol  
B  propanal → propan-1-ol  
C  propanoic acid → propanal  
D  propanone → propan-2-ol
**Free Radicals**

The aim of this activity is to introduce free radicals.

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

![Chemical structures of ethene, ethanol, and chloromethane](image)

During reactions bonds will break and **intermediates** will be formed. For example, when chloromethane reacts, the C — Cl bond can break. The chlorine atom has a higher **electronegativity** - a stronger attraction for the bonding electrons - so this bond will break to produce ions.

During collisions - perhaps with other chloromethane molecules, perhaps with the wall of the container, perhaps with the other reactant - if the collision has sufficient energy and the collision geometry is suitable, then the C — Cl bond may break and the intermediate ions may be formed. The methyl ion is very unstable and, therefore, very reactive.

**Think**

- How many electron pairs surround each carbon atom in all three stable molecules?
- How many electron pairs surround the chlorine atom in the stable chloromethane molecule?
- How many electron pairs surround the oxygen atom in the stable ethanol molecule?

**Notes**

In stable molecules all atoms (apart from hydrogen) will have 4 electron pairs - the **stable octet**. During reactions bonds will break and **intermediates** will be formed. For example, when chloromethane reacts, the C — Cl bond can break. The chlorine atom has a higher **electronegativity** - a stronger attraction for the bonding electrons - so this bond will break to produce ions.
There are many reagents that can react with the methyl ion produced.

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

Overall the reaction would be:

$$ CH_3Cl + NaOH \rightarrow CH_3OH + NaCl $$

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.

Consider the situation described on the previous page.

- Why is the C — Cl bond in the chloromethane the most likely to break during a collision?
- What term is more usually used to describe the “Extra Energy taken in”?
- Where does this energy come from? **Hint:** What were the molecules doing just before they collided? What happens when they collide?
- What term is more usually used to describe the intermediate ions forming?
- What is meant by collision geometry?
- Why is the methyl ion formed so unstable/reactive?
- Why is the chloride ion formed stable?

Consider the situation described above.

- Why is the hydroxide ion considered to be stable?
- What is the name of the alcohol formed?
- Why is this alcohol molecule stable?
- What type of Organic reaction has taken place?
Whilst polar bonds are generally easier to break, non-polar bonds can also break, though extra energy, in the form of light, is often required. When these bonds break, each atom retains its own electron but very unstable, very reactive free radicals are formed.

**Free radicals can be** atoms, or molecules

<table>
<thead>
<tr>
<th>Bond</th>
<th>Electron Pairs</th>
<th>Radical</th>
<th>Energy Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl — Cl</td>
<td>2 Cl•</td>
<td>chlorine radicals</td>
<td>hydroxyl radicals</td>
</tr>
<tr>
<td>H — O — O — H</td>
<td>2 •OH</td>
<td>hydrogen peroxide</td>
<td></td>
</tr>
</tbody>
</table>

Consider the structures shown above.

- How many electron pairs surround each chlorine in the Cl₂ molecule?
- How many electron pairs surround each chlorine in the Cl• radical?
- Does the Cl• radical have a charge? Is it an ion? Explain.
- How many electron pairs surround each oxygen in the H₂O₂ molecule?
- How many electron pairs surround each oxygen in the •OH radical?
- Does the •OH radical have a charge? Is it an ion? Explain.

**Hint:** How many electrons belong to the oxygen?

- Why is it called the hydroxyl radical and not hydroxide radical?
- Why should it be shown as •OH or HO• but not OH• or •HO?

When light of the correct energy strikes a bond, the energy can be absorbed.

\[
\text{Cl} — \text{Cl} \rightarrow 2 \text{Cl•}
\]

This extra energy can cause the bond to break - producing free radicals.

For example, the energy required to break a Cl — Cl bond is equivalent to light of a wavelength of 493.8 nm (1nm = 10⁻⁹ m).

The Br — Br bond is easier to break and would require light of wavelength 618.6 nm.

Energy is inversely proportional to wavelength so

\[
E \propto \frac{1}{\lambda} \quad \text{or} \quad E = \frac{k}{\lambda}
\]

where \( k = \text{constant of proportionality} \)

**Halogen Bond Enthalpies (kJ mol⁻¹)**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Enthalpy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F — F</td>
<td>159</td>
</tr>
<tr>
<td>Cl — Cl</td>
<td>243</td>
</tr>
<tr>
<td>Br — Br</td>
<td>194</td>
</tr>
<tr>
<td>I — I</td>
<td>151</td>
</tr>
</tbody>
</table>

Calculate the constant of proportionality, \( k \), and then use it to calculate the wavelength of light needed to break the I — I and F — F bonds.
⑤ **Free Radical Chain Reaction**

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

In the substitution reaction met earlier:

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

the reaction will be over after the second collision when the products are formed.

When a free radical reacts with another molecule, a *new* free radical is *always* produced. This new free radical can then go on and react to produce another free radical and so the reaction continues ‘forever’ - a *chain reaction*.

For example, the substitution reaction between an alkane and a halogen has a number of steps which will repeat ‘forever’.

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

\[
\begin{align*}
\text{Cl}^- & + \text{ photon (hv)} \\ 
\text{Cl}^- & \rightarrow \text{Cl}^* + \text{Cl}^-
\end{align*}
\]

**Propagation:** *the steps that will see a free radical react but a new free radical produced.*

*First propagation step*

\[
\begin{align*}
\text{H} & - \text{C} - \text{H} + \text{Cl}^- \\ 
\text{H} & - \text{C}^* - \text{H} + \text{H} - \text{Cl}
\end{align*}
\]

methyl radical chlorine atom methyl radical hydrogen chloride

*Second propagation step*

\[
\begin{align*}
\text{H} & - \text{C}^* + \text{Cl}^- - \text{Cl}^- \\ 
\text{H} & - \text{C} - \text{Cl} + \text{Cl}^-
\end{align*}
\]

methyl radical chlorine molecule chloromethane chlorine atom

For most of the time, the high concentration of molecules will ensure that free radicals produced will always react with molecules. Eventually, once the supply of molecules has diminished, there is the possibility that free radicals will collide with other free radicals or with the walls of the container.

**Termination:** *the steps that will see a chain eventually stopped.*

\[
\begin{align*}
\text{H} & - \text{C}^* + \text{Cl}^- \\ 
\text{H} & - \text{C} - \text{Cl} \\
\text{Cl}^* & + \text{Cl}^- \rightarrow \text{Cl}^- - \text{Cl}^-
\end{align*}
\]
Detailed descriptions of the steps involved in a reaction - showing the movement of electrons as bonds break and form - is called a **Reaction Mechanism**. You will be expected to know in some detail this mechanism and the names of the different stages.

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 alkanes. 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,

\[
\text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr} \quad \text{slow, substitution, in light}
\]

\[
\text{C}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_4\text{Br}_2 \quad \text{fast, addition, in dark if necessary}
\]

Write the **Reaction Mechanism** for the reaction between *ethane* and *bromine*.

Show, and label, the **initiation**, **propagation** and **termination** steps.

Show, using **single head** arrows, the movement of electrons.

**Think**

Consider the mechanisms you have seen (including the reaction between chloromethane and sodium hydroxide).

- Why are **single head** arrows used in some mechanisms but **double headed** arrows in others to show the movement of electrons?
- How many chains are started by the initiation step?

Only a very small proportion of halogen molecules are broken apart by the photons of light.

- Why does this not matter?

The equations for the free radical reactions do not show the by-products of these reactions.

- Give examples of these by-products and explain how they are formed.
SELF CHECK

Q1. Which of the following statements about a free radical is correct?
A it has a lone pair of electrons
B it has a stable octet
C it has a single unpaired electron
D it has lost an electron to form an ion

Q2. Which of the following bonds is most likely to break to form free radicals
A C — H
B O — H
C C — O
D O — O

Q3. Which of the following substances could not be produced in the chain reaction between ethane and chlorine.
A HCl
B C₂H₅Cl
C C₂H₅Cl
D C₄H₁₀

Q4. Which of the following represents an initiation step in a chain reaction?
A Cl₂ → 2Cl•
B CH₃• + CH₃• → C₂H₆
C CH₄ + Cl• → CH₃Cl + H•
D CH₃• + Cl₂ → CH₃Cl + Cl•

Q5. The reaction between chlorine and ethane to give chloroethane is an example of a chain reaction.
Which of the following is a propagation step in this reaction?
A Cl₂ → Cl• + Cl•
B C₂H₅• + Cl• → C₂H₅Cl
C C₂H₅• + C₂H₅• → C₄H₁₀
D C₂H₅• + Cl₂ → C₂H₅Cl + Cl•

Questions 6 & 7 refer to the following table of Bond Enthalpies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Enthalpy/kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br—Br</td>
<td>194</td>
</tr>
<tr>
<td>H—Br</td>
<td>362</td>
</tr>
<tr>
<td>C—H</td>
<td>414</td>
</tr>
<tr>
<td>C—Br</td>
<td>285</td>
</tr>
</tbody>
</table>

Q6. Which bond would require light of lowest wavelength to break?
A Br — Br
B H — Br
C C — H
D C — Br

Q7. What is the enthalpy change for the following reaction?

\[
\text{H} - \text{H} \\
\text{H} - \text{C} - \text{C} - \text{H} + \text{Br} - \text{Br} \\
\text{H} - \text{H} \\
\text{H} - \text{C} - \text{C} - \text{Br} + \text{H} - \text{Br} \\
\text{H} - \text{H}
\]
A -1255 kJ mol⁻¹
B -39 kJ mol⁻¹
C +39 kJ mol⁻¹
D +1255 kJ mol⁻¹

Q8. Which of the following will not be a termination step in a chain reaction?
A H• + Cl• → HCl
B Cl• + Cl• → Cl₂
C CH₃• + CH₃• → C₂H₆
D CH₃• + Cl• → CH₃Cl
**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.

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 macromolecules.

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

- **Superoxide**
  \[
  \text{\text{O}_2^\cdot -}
  \]

- **Peroxide**
  \[
  \text{\text{O}_2^{2\cdot -}}
  \]

- **Hydroxyl**
  \[
  \text{\text{OH}^\cdot}
  \]

In addition, damage can also be caused by ‘*excited*’ oxygen molecules that have absorbed extra energy but have not formed a radical.

These molecules are often referred to as a ‘*singlet*’ oxygen and denoted by \( ^1\text{O}_2 \) or \(*\text{O}_2 \).

Consider the information given above.

- List the main external processes that lead to the production of radicals.

  Mitochondria convert energy into a usable form (ATP) but produce *hydrogen peroxide* as a by-product in about 1% of these reactions.

  - What is the formula for *hydrogen peroxide*? What enzyme is present in most cells to break down *hydrogen peroxide*?
  - Which of the *reactive oxygen species* is most commonly produced?
  - What is meant by the phrase ‘*macromolecules*’?
  - Give examples of some of the types of macromolecules found in the human body.
  - What is the difference between ‘*macromolecules*’ and ‘polymers’?
Though they have beneficial activities - for example, white blood cells produce radicals to help destroy invading pathogens - reactive oxygen species can also be toxic to cells. Macromolecules such as lipids (derived from fatty acids), proteins and nucleic acids (DNA) are particularly vulnerable to damage through a process known as lipid peroxidation.

As with all radical reactions the ‘product’ always includes a new radical that can continue the chain reaction. This can involve reaction with a neighbouring phospholipid (leading to further damage to membranes), or with proteins or with molecules of DNA.

Rearrangement of the lipid can also take place leading to the formation of complex aldehydes called malondialdehyde and 4-hydroxy-2-nonenal which has been linked to a variety of medical conditions such as Alzheimer’s disease, Cancer, Cardiovascular diseases, Diabetes, Liver disease and Parkinson’s disease.

Malondialdehyde can undergo ‘normal’ oxidation to form the diacid malonic acid. Draw the structural formulae for this acid and the diacid that could be formed from 4-hydroxy-2-nonenal.

What to do

Draw full structural formulae for both of the aldehydes mentioned above.

For 4-hydroxy-2-nonenal, work out which part of the name describes the position of the alcohol part and the position of the alkene part.
Antioxidants

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

A food manufacturer's goal is to deliver a product that looks good, tastes fresh and is consistent time and time again. Lipid oxidation (fats & oils) is a common factor that causes food products to turn rancid and/or have color changes.

If fats oxidise, they produce “off” odours and flavours (stale, rancid odors). Often, if fats oxidise, vitamins also oxidise and lose their activity.

If pigments oxidise, they can change colour completely. For example, red meat turns gray when the myoglobin pigment oxidises. In this case, the product is not unsafe; it just looks less appealing.

Antioxidants can be classified as one of two types: ‘traditional’ reducing agents or free radical scavengers.

Wine makers, for example, use SO2 and/or sulphites (SO2 → SO3^-2 in water) to slow down or prevent oxidation. Sausages and other processed meats similarly use sulphites or nitrites as preservatives:

\[
\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} \\
\text{NO}_2^- \rightarrow \text{NO}_3^-
\]

Care must be taken as too high a level of sulphites, in particular, introduces an unpleasant taste and can cause asthma attacks.

Ascorbic acid can act as a traditional reducing agent, though it also scavenges for free radicals.

\[
\text{ascorbic acid} \quad \rightarrow \quad \text{dehydroascorbic acid}
\]

What to do

Complete the ion-electron \(\frac{1}{2}\) equations for the three reactions mentioned above. Use molecular formulae for ascorbic acid and dehydroascorbic acid.
As previously mentioned, the main problem when trying to react away radicals is that one of the products is also always a radical. The trick is to form a stable radical that is much less likely to react and allow you, therefore, to stop the chain reaction.

There are a number of features that can help make a radical more stable:

1. **multiple substituents** - more groups attached to the atom with the single electron, e.g.

   ![Methyl radical](image1)  \( < \) ![Primary radical](image2)  \( < \) ![Secondary radical](image3)  \( < \) ![Tertiary radical](image4)

   *Methyl radical*  
   *Least stable*  
   *Primary radical*  
   *Secondary radical*  
   *Tertiary radical*  
   *Most stable*

   **Radical stability increases in the order methyl < primary < secondary < tertiary**

2. **conjugated systems** - alternating double and single bonds, e.g.

   ![Conjugated systems](image5)

   the position of the double bond and the site of the single electron can change so effectively the burden is shared.

   **Benzene rings** can have a particularly strong stabilising effect on radicals.

3. **hydrogen donors** - these are groups (usually polar) that can easily lose a hydrogen atom to a radical, e.g.

   ![Hydrogen donors](image6)

   A molecule of ascorbic acid *(Vitamin C)* can react with a radical but will itself become an ascorbyl radical.

   However, the ascorbyl radical can take advantage of its **conjugated system** to share the ‘burden’ of coping with a single electron and will be stable enough to not need to react further so the chain is effectively stopped.

   The ascorbyl radical will, however, often go on and scavenge another radical making it even more effective as an **antioxidant.**
All the above molecules are natural antioxidants. Phenolic antioxidants can inhibit free radical formation and/or interrupt propagation in the oxidative chain reaction. Fat-soluble vitamin E (α-tocopherol) and water-soluble vitamin C (L-ascorbic acid) are both effective. Plant extracts, generally used for their flavouring characteristics, often have strong H-donating activity thus making them extremely effective antioxidants. Other molecules rely on their high level of conjugation to form stable radicals.

Consider the information given above and on the previous page.

- What is meant by ‘natural’ as in ‘natural antioxidants’?
- What is meant by ‘phenolic’ as in ‘phenolic antioxidants’?
- Which of the antioxidants has the most hydroxyl groups?
- Which of the antioxidants is the most phenolic?
- Which of the antioxidants contains a carboxylic group?
- Lycopene has the highest level of conjugation. How do you think the level of conjugation is ‘measured’?
- Which of the antioxidants has the next highest level of conjugation?
- Lycopene is fat soluble. Which of the other antioxidants would you expect to be most likely to be fat soluble? Explain.
- Vitamin C (ascorbic acid) is water soluble. Which of the other antioxidants would you expect to be most likely to be water soluble? Explain.
**Free Radical Scavengers**

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

Free Radical Scavengers are molecules that can react with free radicals to form stable molecules and prevent chain reactions. They are found naturally in living organisms and, hence, in many foods but can also be added to other products such as cosmetics and plastics.

<table>
<thead>
<tr>
<th>Active Ingredient</th>
<th>Type of UV radiation blocked</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aminobenzoic acid</td>
<td>UV-B</td>
</tr>
<tr>
<td>Avobenzone</td>
<td>UV-A</td>
</tr>
<tr>
<td>Cinoxate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Dioxybenzone</td>
<td>UV-B, UV-A</td>
</tr>
<tr>
<td>Homosalate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Menthyl anthranilate</td>
<td>UV-A</td>
</tr>
<tr>
<td>Octocrylene</td>
<td>UV-B</td>
</tr>
<tr>
<td>Octyl methoxycinnamate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Octisalate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Oxycbenzone</td>
<td>UV-B, UV-A</td>
</tr>
<tr>
<td>Padimate O</td>
<td>UV-B</td>
</tr>
<tr>
<td>Phenylbenzimidazole sulfonic acid</td>
<td>UV-B</td>
</tr>
<tr>
<td>Sulisobenzene</td>
<td>UV-B, UV-A</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>UV-A/B, broad spectrum</td>
</tr>
<tr>
<td>Trolamine salicylate</td>
<td>UV-B</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>UV-A/B, broad spectrum</td>
</tr>
</tbody>
</table>

As mentioned previously, UV light can initiate the formation of free radicals which, in the body, leads to cell damage (aging of the skin) and could ultimately lead to damage to DNA and the formation of cancer.

Most ingredients in Sun-Blocks try and prevent the UV light getting through and a whole range of molecules are needed as each molecule can only absorb a certain part of the UV spectrum.

Many cosmetic products have started to include natural oxidants/free radical scavengers in skin products in particular and claim that they can give significant protection against skin aging. When added to Sun-Blocks they can also help extend the protection offered by the ‘blocking’ molecules.

The body also produces melatonin - the hormone that controls our day-night cycle (biological clock). However, it is also been found to be a powerful free-radical scavenger and wide-spectrum antioxidant that is twice as active as Vitamin E - previously considered to be the most effective antioxidant.

Though triggered by changes in light levels, melatonin is produced at night and helps us sleep. Human infants’ melatonin levels become regular in about the third month after birth. As children become teenagers, the nightly schedule of melatonin release is delayed, leading to later sleeping and waking times. Human melatonin production decreases as a person ages.

Polymers are considered to get weathered due to the direct or indirect impact of heat and ultraviolet light. Polymers containing peroxide — O — O — links and carbonyl C = O groups are particularly vulnerable to UV initiated radical oxidation which can lead to breaking of chains and unwanted cross-linking.

Photo-oxidation reduces the polymer’s molecular weight. As a consequence of this change the material becomes more brittle, with a reduction in its tensile, impact and elongation strength. Discoloration and loss of surface smoothness accompany photo-oxidation. Dye molecules are added to try and absorb UV while antioxidants such as phenol are used to inhibit the formation of radicals.
### Self Check

**Q1.** Which of the following is unlikely to cause the formation of free radicals?
- A. overexposure to the sun
- B. eating fruits and vegetables
- C. pollution
- D. tobacco smoke

**Q2.** What is a molecule that has the ability to prevent oxidation better known as?
- A. a free radical
- B. a nucleotide
- C. an antioxidant
- D. an electron

**Q3.** Phenols can act as antioxidants because
- A. they are acidic
- B. they undergo addition reactions
- C. they are free radical scavengers
- D. they are easily oxidised

**Q4.** Which part of a cell is responsible for producing damaging free radicals?
- A. mitochondria
- B. cell membrane
- C. nucleus
- D. golgi body

**Q5.** Vitamin C, vitamin E and sulphites are all
- A. flavour enhancers
- B. antimicrobial agents
- C. emulsifying agents
- D. antioxidants

**Q6.** Melatonin is described as a “wide-spectrum antioxidant”. This means that
- A. it absorbs light of all wavelengths
- B. it can react in different ways
- C. it can react with a variety of different molecules
- D. it is a very large molecule

**Q7.** The triphenylmethyl radical is considered to be one of the most stable formed.

Which of the following gives the best explanation for this stability?
- A. there are 3 groups attached to the carbon
- B. the molecule has a large molecular weight
- C. the single electron can move to different places within the molecule
- D. it will be easy to remove a hydrogen atom from one of the rings

**Q8.** Which part of the phospholipid molecule that makes up cell membranes is most vulnerable to attack by a free radical?
- A. the phosphate group
- B. any saturated fatty acid
- C. the glycerol section
- D. any unsaturated fatty acid
CfE New Higher - Unit 2- Topic 5 Study Guide  - Organic 1

5.3

HOME PRACTICE

Q1. Carbon monoxide gas is produced as a result of the incomplete combustion of fuels.

The amount of carbon monoxide in the atmosphere is controlled by a series of free radical reactions.

a) What is meant by the term free radical?  

b) Why do free radicals form in the atmosphere?  

c) The equation shows one of the steps in the free radical chain reaction which controls the level of carbon monoxide.

\[ \text{CO} + \text{HO}\cdot \rightarrow \text{CO}_2 + \text{H}\cdot \]

What term describes this type of step in the free radical chain reaction?  

d) Carbon monoxide can be used to produce the gas tricarbon dioxide, \( \text{C}_3\text{O}_2 \), a substance used to bind dyes to natural fur.

Draw a structural formula for tricarbon dioxide.  

Q2. Suncreams contain antioxidants.

a) The antioxidant, compound A, can prevent damage to skin by reacting with free radicals such as \( \text{NO}_2\cdot \).

\[ \text{Compound A} \]

i) Why can compound A be described as a free radical scavenger in the reaction shown above?  

ii) What atom was most likely originally attached to the carbon circled?  

iii) What feature in the structure of compound A allows it to form a stable radical.  

b) Another antioxidant used in skin care products is vitamin C, \( \text{C}_6\text{H}_8\text{O}_6 \).

An incomplete equation for the reaction of Vitamin C is shown below.

\[ \text{C}_6\text{H}_8\text{O}_6 \text{ (aq)} \rightarrow \text{C}_6\text{H}_6\text{O}_6 \text{ (aq)} \]

i) How can you tell that this is an oxidation reaction?  

ii) Copy and complete the ion-electron equation for the oxidation of vitamin C.  

Total (9)