11 Aldehydes and Ketones

Note: Aldehydes and ketones are not mentioned in the syllabus. However, they are products in the oxidation of alcohols – which is in the syllabus. Hence they are covered briefly here.

Functional group

Aldehydes and ketones both contain the **carbonyl functional group**. They differ in what is attached to this carbonyl group.

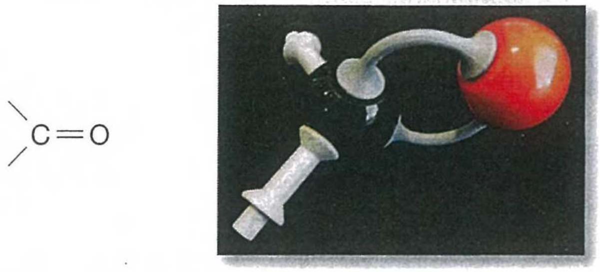
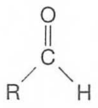


Figure 11.1 Carbonyl group.

Aldehydes

Aldehydes (also called alkanals) are organic compounds with general formula RCHO where R is an alkyl chain, e.g. C_3H_7. In aldehydes the **carbonyl group is on a terminal (end) carbon atom of a chain.**



Aldehydes can be formed by the oxidation of a primary alcohol. The common names of aldehydes are taken from the names of the acids they can be converted into by the process of oxidation.

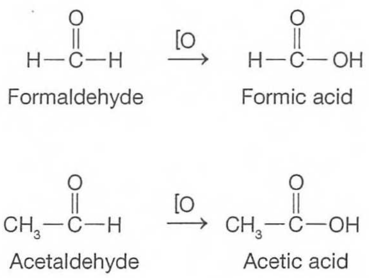


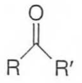
Figure 11.2 Examples of aldehydes, using common names, showing the carboxylic acids they form on oxidation.

IUPAC naming of aldehydes

1. Choose the longest unbranched chain containing the carbonyl group.
2. Number from the C with the attached =O.
3. Replace the 'e' at the end of the alkane with 'al'. For example, formaldehyde contains one C and is called methanal, acetaldehyde contains two C's and is called ethanal.

Ketones

Ketones (also called alkanones) are organic compounds with general formula RCOR′ where R and R′ are alkyl chains. In ketones the carbonyl group is on a carbon atom which is not in a terminal position (not at either end). The simplest ketone, acetone (or propanone) has three carbon atoms.



IUPAC naming of ketones

1. Choose the longest unbranched chain containing the carbonyl group.
2. Number so that the C with the attached =O has the smallest possible number.
3. Replace the 'e' at the end of the alkane with 'one'. For example, acetone is called propanone and pentanone can be pentan-2-one or pentan-3-one depending on the position of the carbonyl group.

Ketones can be **formed by** the oxidation of secondary alcohols. Ketones cannot be oxidised to acids.

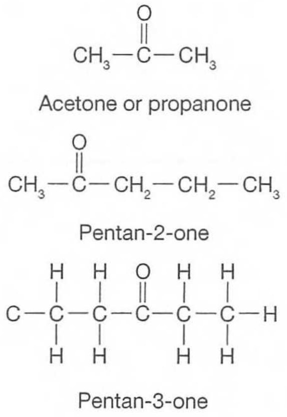


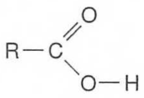
Figure 11.3 Examples of ketones (alkanones).

QUESTIONS

1. Identify the functional group in aldehydes and ketones.
2. Distinguish between aldehydes and ketones.
3. Name the following substances.
   (a) $CH_3CH_2CH_2COCH_3$
   (b) $CH_3CH_2CH_2CH_2CH_2COCH_3$
   (c) $CH_3CH_2CH_2CHO$
4. Add aldehydes and ketones to the table in Question 4 in Chapter 10.

6 Carboxylic Acids

The general structure of **carboxylic acids** (also called alkanoic acids) can be shown as:



Where R is a hydrogen atom or an alkyl group.

Carboxylic acids are organic compounds which contain a –**COOH group**. The COOH group is called a **carboxyl group**.

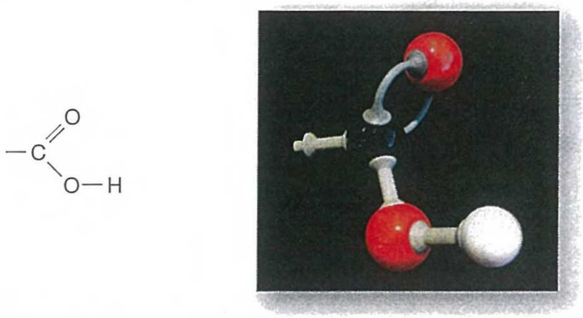


Figure 6.1 Carboxyl group.

In carboxylic acids, the carboxyl group is attached to a hydrogen atom or to a saturated carbon chain (an alkyl group) with the formula C_nH_{2n+1}. The suffix –anoic is used, for example ethanoic acid.

The carboxyl group

The carboxyl group COOH is the functional group for carboxylic acids. In the carboxyl group, a carbon atom is bonded to two different oxygen atoms, one by a single C–O bond and the other by a double C=O bond.

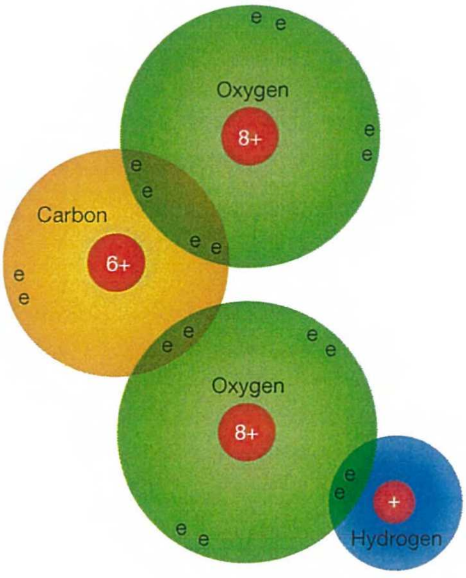


Figure 6.2 Structure of carboxyl group.

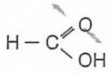
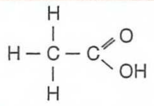
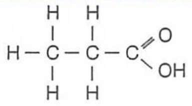
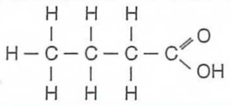
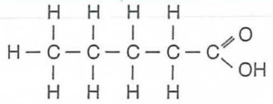
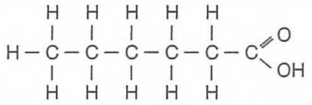
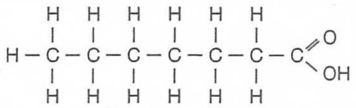
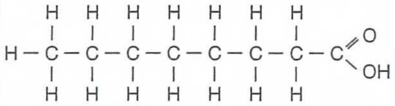
Examples of carboxylic acids

Methanoic acid, HCOOH is the simplest carboxylic acid. Pure methanoic acid has a pungent irritating odour and can blister the skin. Methanoic acid is also called formic acid as it was first isolated from ants (Latin: formica = ants). Ant stings can be neutralised with sodium hydrogen carbonate. Methanoic acid is used as a preservative and an antibacterial agent.

Ethanoic acid, CH_3COOH is also called acetic acid and is the main component of vinegar. Vinegar is approximately 4% to 8% acetic acid. It is used to flavour and preserve food. Ethanoic acid is corrosive, and has a sour taste and a strong odour. It is used extensively in the production of glues and synthetic fibres.

Examples of carboxylic acids are shown in Table 6.1.

Table 6.1 Carboxylic acids.

Name	Structural formula	Molecular formula
Methanoic acid		HCOOH
Ethanoic acid		CH_3COOH
Propanoic acid		C_2H_5COOH
Butanoic acid		C_3H_7COOH
Pentanoic acid		C_4H_9COOH
Hexanoic acid		$C_5H_{11}COOH$
Heptanoic acid		$C_6H_{13}COOH$
Octanoic acid		$C_7H_{15}COOH$

Longer chain alkanoic acids are called fatty acids and are components of the lipids (fats and oils) in living things.

As with other chemicals which are important in industry, some of the carboxylic acids are known by common names as well as their IUPAC names. For example, see Table 6.2.

Table 6.2 Names of acids.

Formula	IUPAC name	Common name
$HCOOH$	Methanoic acid	Formic acid
CH_3COOH	Ethanoic acid	Acetic acid
C_2H_5COOH	Propanoic acid	Propionic acid
C_3H_7COOH	Butanoic acid	Butyric acid
$C_{11}H_{23}COOH$	Dodecanoic acid	Lauric acid

Properties of carboxylic acids

- Carboxylic acids are organic acids with **strong odours**, e.g. acetic acid (vinegar) and butyric acid (smells like vomit). They can be identified by techniques such as infra-red spectroscopy.
- Carboxylic acids are **more polar** than alcohols, and they also have **higher melting and boiling points**, due to the presence of the carboxyl group which forms extensive hydrogen bonds.
- They are **weak acids**. In water solution they release hydrogen ions from the COOH group to a water molecule. For example:

  $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

  This can also be written as:

  $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

  Ethanoic acid + water $\rightleftharpoons$ ethanoate ion + hydronium ion

Notice that the ion produced when ethanoic acid ionises, is called an ethanoate ion (CH_3COO^-) and it has a single negative charge.

Reactions of carboxylic acids

- **Reactions with metals**

Carboxylic acids react with active metals to produce a salt and hydrogen. For example:

$2CH_3COOH(aq) + Mg(s) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$

Ethanoic acid + magnesium → magnesium ethanoate + hydrogen

- **Reactions with metal hydroxides**

Metal hydroxides, e.g. sodium hydroxide, are bases so they can be **neutralised** by carboxylic acids.

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

Ethanoic acid + sodium hydroxide → sodium ethanoate + water

As with other acid/base reactions this can be represented by the ionic equation:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

- **Reactions with carbonates and hydrogen carbonates**

Organic acids react with carbonates and hydrogen carbonates to produce water, carbon dioxide and a salt. (You will recall that inorganic acids, e.g. HCl also react in this way.) For example:

$2CH_3COOH(aq) + Na_2CO_3(aq) \rightarrow 2CH_3COONa(aq) + H_2O(l) + CO_2(g)$

- **Reactions with alcohols and amines**

Carboxylic acids react with alcohols and with compounds called amines – you will learn about those reactions soon.

Strength of carboxylic acids

The strength of an acid is determined by how easily it can release (donate) protons when it goes into solution. The easier the protons (H^+ ions) are released into solution, the more acidic the molecule.

The carboxyl group (COOH) contains a double bonded oxygen atom (=O) and a single bonded hydroxyl group (–OH). The hydroxyl group can ionise and release hydrogen ions (H^+) in solution, forming a conjugate base ($-COO^-$). This ability to release hydrogen ions makes it an acid.

Carboxylic acids are described as **weak acids** because they do not ionise completely. Most of the acid (more than 90%) is present as un-ionised molecules – the percentage is affected by concentration and temperature.

We can show its ionisation as an equilibrium equation where the equilibrium lies far to the left.

$AH + H_2O \rightleftharpoons A^- + H_3O^+$

or more simply as:

$AH(aq) \rightleftharpoons A^-(aq) + H^+(aq)$

In these equations A stands for the anion.

If you **substitute an atom or group of atoms** for a hydrogen in a carboxylic acid you affect its strength. Replacing a hydrogen atom with a group such as CH_3 makes the acid weaker, because such groups will tend to push electrons away.

Replacing a hydrogen atom with a group or atom which can withdraw electrons, pulling them away from the COO^- end of the molecule will make the acid stronger. An atom such as chlorine (or other halogens) is electronegative, so its addition will have this effect, making the acid stronger, especially if it is attached not far from the $-COO^-$ group.

CH_3-COOH

$Cl-CH_2-COOH$

$Cl_3-C-COOH$

↓ Increasing acidity

7 Esters

An ester is an organic compound with the functional group –COO– and general formula RCOOR′ where R and R′ are carbon chains.

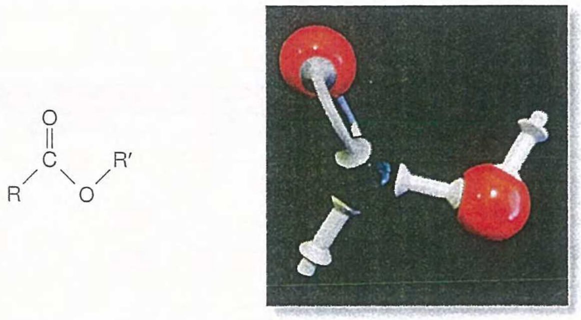


Figure 7.1 The general formula and model of an ester.

Some examples of esters are shown in Figure 7.2.

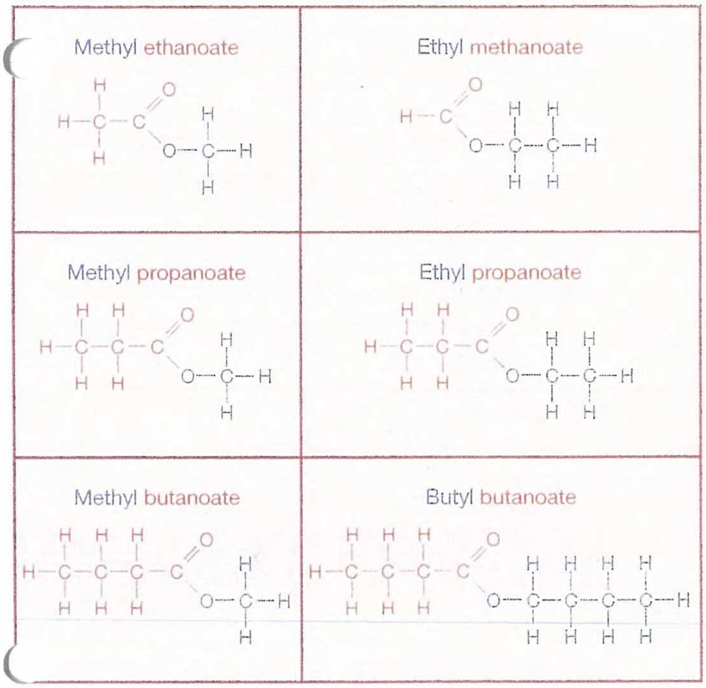
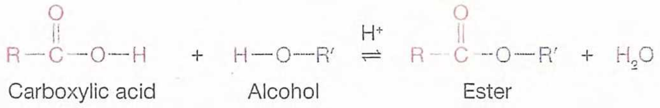


Figure 7.2 Examples of esters.

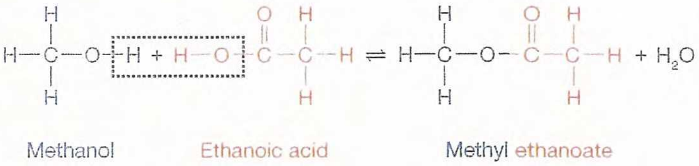
You will understand the naming of esters better when you see how esters are made – they are produced by the reaction of a **carboxylic acid** and an **alcohol**. The process of producing an ester from a carboxylic acid and an alcohol is called **esterification**.

During esterification, the **–OH group from the –COOH** (carboxyl group) of a carboxylic acid combines with the **H from the –OH** (hydroxyl group) of an alcohol to produce a molecule of water.

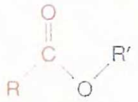


(Note that this is different from inorganic chemistry – where the H^+ from an acid combines with the OH^- from an alkali during neutralisation.)

For example:

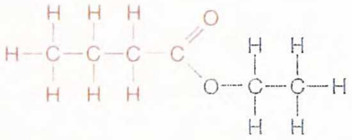


Now, if you look again at the structure of an ester, you will see that the remains of the carboxylic acid can readily be identified because it contains a double bonded oxygen atom (=O). The single bonded O atom from the alcohol unites with what is left of the acid. So in the figure below, RCO is from the acid and R′O is from the alcohol.



The tricky part when naming esters is to remember that the part from the alcohol is always mentioned first, even though the acid fragment may be drawn first.

Here is another example – ethyl butanoate.



This would be made by reacting ethanol with butanoic acid.

Ethanol + butanoic acid → ethyl butanoate + water

$C_2H_5OH(aq) + C_3H_7COOH(aq) \rightarrow C_3H_7COOC_2H_5(l) + H_2O(l)$

Properties of esters

- **Occurrence** – Many esters occur naturally, in living things. Fats and oils are esters and many have a fruity odour and give perfume to flowers and fruits.
- **State** – Most esters have low melting points so are liquids at room temperature. Larger esters are solids due to their stronger intermolecular forces.
- **Solubility** – Esters with very small molecules are soluble in water, but, as with other series, solubility decreases as the size of the molecule increases.
- **Polarity** – The ester functional groups are polar, but not as polar as alcohols. They cannot form hydrogen bonds with other ester molecules, although they can form hydrogen bonds with water molecules.

8 Esterification

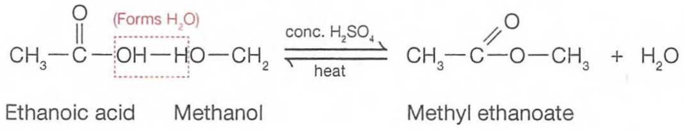
Esterification is the production of an ester by the reaction between an alcohol and a carboxylic acid. Water is produced as a by-product so this reaction is sometimes called a condensation reaction or a dehydration reaction.

The **general equation** for esterification is:

Carboxylic acid + alcohol $\rightleftharpoons$ ester + water

$$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$

For example, methanol reacts with ethanoic acid to produce methyl ethanoate and water. Concentrated sulfuric acid is used as a **catalyst**. It absorbs water, pushing the equilibrium to the right.



$$CH_3COOH + HOCH_3 \xrightleftharpoons[\text{heat}]{\text{conc. } H_2SO_4} CH_3COOCH_3 + H_2O$$

Refluxing

This reaction is carried out by **refluxing**. The reactants are heated in a flask, placed in a warm water bath, with a cooling condenser attached vertically to the top of the flask. Using this technique, the reaction can be carried out at a higher temperature than would otherwise be possible. The reactants and products all tend to be volatile, so heating would lead to them vaporising into the environment. Using the condenser allows volatile substances to be cooled so they recondense and fall back into the flask instead of being released into the environment.

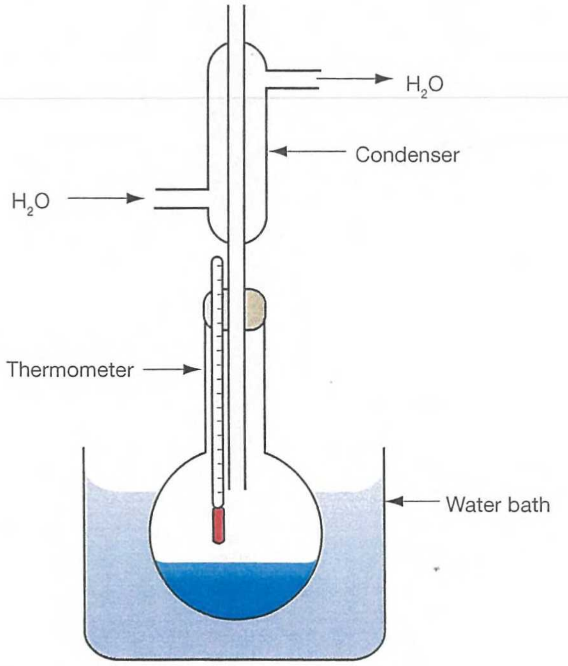


Figure 8.1 Esterification.

Using the condenser is essential, as some organic chemicals have a very strong odour, which can be unpleasant, e.g. butanoic acid smells rather like vomit, and some are a health hazard – they may cause headaches and irritate the respiratory system. Also many are flammable, so they could become a fire hazard if released into the environment.

QUESTIONS

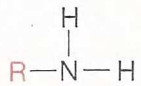
1. (a) What is esterification?
   (b) Write the general equation for this process, indicating from which reactants the water is produced.
   (c) Write a word equation for the production of the ester propyl methanoate.
2. (a) Outline the meaning of the term refluxing.
   (b) In Figure 8.1, why is the condenser connected up so that water enters the bottom of the condenser?
   (c) What is the purpose of the water in the condenser jacket?
   (d) Does the water in the condenser jacket mix with the vapour coming out of the flask?
   (e) Explain the advantage of using reflux when an ester is being produced.
3. Name the esters produced by the following reactions.
   (a) Propanol and ethanoic acid.
   (b) Methanol and butanoic acid.
   (c) Ethanol and propanoic acid.
4. Copy and complete the table to show formulas, names and odours of some esters. You may need to research the aromas.

Formula	Name	Aroma
$HCOOCH_2CH_3$		
	Methyl butanoate	
		Pineapple
$CH_3COO(CH_2)_4CH_3$		
	Pentyl butanoate	Apricot
$CH_3COO(CH_2)_7CH_3$		

5. Check your knowledge with this quick quiz.
   (a) Identify a use of esters.
   (b) Name the ester made from pentanoic acid and butanol.
   (c) Write the structural formula for pentyl propanoate.
   (d) Identify the term for the production of esters.
   (e) Esters are produced using a technique called
   ....
   (f) Name the substance used as a catalyst during esterification.

9 Amines

An **amine** is an organic compound which contains the functional group $-NH_2$ attached to a hydrocarbon chain or ring. The general formula for an amine is $R-NH_2$.



$R-NH_2$

Amines are named using the suffix -amine. Some examples are shown in Figure 9.1.

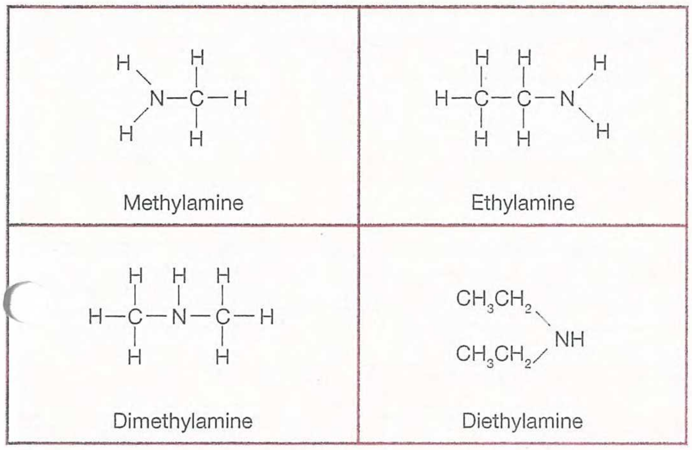


Figure 9.1 Examples of amines.

As with alcohols, amines can be **primary, secondary or tertiary** amines depending on the number of hydrocarbon groups attached to the nitrogen atom.

Properties of amines

- Amines **are polar molecules.**
- Amines have **lower boiling points than similar sized alcohols.** They can form hydrogen bonds as well as dipole-dipole forces and dispersion forces. However, their hydrogen bonding is not as strong as in alcohols because there are fewer lone pairs on the N atom.
- The small molecule amines are **soluble in organic solvents**, and **also in water**, because they can form hydrogen bonds. However, solubility decreases as the chain gets longer.

  $CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$
- Amines are **weak bases** (like ammonia).

  $CH_3NH_2 + HCl \rightleftharpoons CH_3NH_3^+ + Cl^-$
- Amines have a similar smell to ammonia. Larger amines have a sickly 'fishy' smell.

Making amines

Amines are formed from ammonia (NH_3) when one or more of its hydrogen atoms is replaced by a hydrocarbon group. They can be made by a substitution reaction between ammonia and a haloalkane. For example:

Chloroethane + ammonia → ethylamine + hydrogen chloride

$$C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$$

Importance of amines

Amines are **important in biology**. The **amino acids** which make up proteins have an amine group, so amines are found in all living organisms. Many neurotransmitters in the body are amines, e.g. serotonin, histamine and dopamine. Amines are also important in determining the 3-D structure of proteins.

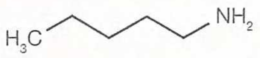
Foods also contain amines, e.g. histamine in wine and phenylethylamine in chocolate. Amines are present naturally in some foods such as fruits and vegetables. In other foods, e.g. meat, dairy products, alcoholic drinks and fermented foods, amines are usually formed by the action of bacteria.

Amines in foods we eat are broken down with the help of a special enzyme. In some people, genetic variations mean that this enzyme is missing, or its action may be blocked. When this happens, the amine called tyramine builds up in the body and can cause a range of symptoms including headaches, skin rashes, diarrhoea and aggressive behaviour disorders.

Many **drugs** used by doctors today have been designed to mimic or interfere with amine neurotransmitters, e.g. antihistamines used to relieve allergic reactions. The drugs morphine, codeine and heroin are all tertiary amines. Nicotine and caffeine also contain amine groups.

QUESTIONS

1. What is an amine?
2. Name and state the molecular formula for each of the following amines.
   (a) $CH_3-CH_2-CH_2-NH_2$
   (b)



   (c)

3. Research uses for two named amines.
4. Check your knowledge with this quick quiz.
   (a) What is the functional group of an amine?
   (b) How are amines formed?
   (c) Amines are (acidic/basic/neutral).
   (d) Amines are (polar/non-polar).
   (e) Are amines soluble?

10 Amides

Amides are organic compounds which contain the $-CONH_2$ group.

Amides are **formed from carboxylic acids**. To produce an amide, the carboxyl group (COOH) has its OH replaced by a $-NH_2$ group.

Amides are **named** by replacing the -oic suffix of the carboxylic acid by -amide.

Table 10.1 Examples of amides.

Amide	Formula	Produced from
Methanamide	$HCONH_2$	Methanoic acid
Ethanamide	CH_3CONH_2	Ethanoic acid
Propanamide	$C_2H_5CONH_2$	Propanoic acid

Properties of amides

- Amides have **high melting points** because of the presence of hydrogen bonds.
- Amides are **soluble in water** as they form hydrogen bonds with water molecules.
- Amides are **neutral** to litmus paper. Although they contain a NH_2 group, they do not act as bases.
- Amides can be **reduced** to form amines. For example:

  $CH_3CONH_2 + 4H \rightarrow CH_3CH_2NH_2 + H_2O$

  Ethanamide Ethylamine

Test for an amide

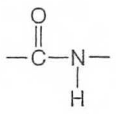
To test an unknown organic chemical in order to see if it is an amide, you add sodium hydroxide solution and then heat. If the unknown chemical gives off ammonia on heating, but not when cold, then it is an amide. Ammonia is detected by its characteristic odour and it also turns red litmus paper blue.

Uses of amides

Amides are used extensively in industries such as in the manufacture of plastics, rubber, paper, crayons, pencils and inks, explosives, adhesives and in water and sewage treatment. They are also used as a coating for many household appliances.

Polyamides

Polyamides are polymers made of amide groups ($-CONH_2-$) linked together to form a polymer. The amide groups are linked together by what is called an amide link – and it is also called a peptide bond.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-$$

Figure 10.1 Amide link (peptide bond).

Two important polymers made with amide links are nylon and Kevlar.

QUESTIONS

1. (a) What is an amide?
   (b) Identify two differences between an amine and an amide.
   (c) Name two amides and state the molecular formula for each.
2. Outline the identification test for an amide.
3. Check your knowledge with this quick quiz.
   (a) Amides tend to be (soluble/insoluble) in water.
   (b) When an amide is reduced it forms an ....
   (c) Amides are (acidic/basic/neutral) to indicators.
   (d) Amides can be identified by the release of .... when dilute .... is added and the reacting chemicals are heated.
4. Copy and complete the table to summarise information about the homologous series you have studied.

Homologous series	Functional group	General formula	Name of example	Formula of example
Alcohol				C_2H_5OH
Carboxylic acid		R–COOH		
Ester			Ethyl methanoate	
Amine	$-NH_2$			
Amide				

12 Identifying Types of Organic Compounds

As you have seen with your studies so far on organic chemistry, functional groups are specific groups of atoms that occur within molecules of different types of organic compounds. These functional groups undergo particular reactions, no matter how big or small the rest of the molecule is. They determine the characteristics and chemical activity of organic molecules.

In organic molecules, the functional groups are less stable than the carbon backbone to which they are attached, so it is the functional group which is most likely to be involved in any chemical reactions.

Looking at the organic compounds you have studied so far during this course, we can summarise some of the chemical reactions involving functional groups that can be used to distinguish between them (see Table 12.1).

Note that oxidation/reduction reactions are not included here, they will be covered in the next chapter.

Table 12.1 Distinguishing tests for organic compounds.

Series and general formula	Distinguishing test
Alkane C_nH_{2n+2}	Does not readily decolourise bromine water.
Alkene C_nH_{2n}	Readily decolourises bromine water, from yellow/brown to colourless, even in the dark.
Alcohol $C_nH_{2n+1}OH$	React with metallic sodium, producing hydrogen gas, e.g. $2C_2H_5OH(aq) + 2Na(s) \rightarrow 2C_2H_5ONa(aq) + H_2(g)$
Carboxylic acid $C_nH_{2n+1}COOH$	Effect on indicators, e.g. turn blue litmus red and no effect on red litmus. React with sodium hydrogen carbonate, producing carbon dioxide gas, which turns limewater milky. $CH_3COOH(aq) + NaHCO_3(aq) \rightarrow CH_3COONa(aq) + CO_2(g) + H_2O(l)$
Amines R–NH_2	Add nitrous acid (HNO_2): With a primary amine (RNH_2) nitrogen is released – a colourless, odourless gas.
Amides R–$CONH_2$	Add dilute sodium hydroxide and heat. An amide will give off ammonia gas when the reactants are heated, but not when cold. Detect the ammonia gas by smell and it also turns red litmus paper blue. $NH_3(g) + H_2O(l) \rightarrow NH_4^+OH(aq)$ $NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
Aldehydes RCHO and Ketones RCOR′	Aldehydes can be oxidised to form carboxylic acids which can be detected by using indicator changes. Ketones cannot be oxidised to acids.

QUESTIONS

1. Reactions with acids and bases can be used to distinguish some types of organic compounds. Identify three examples of this.
2. Explain the importance of the functional group to the chemical characteristics of an homologous series.
3. (a) What is oxidation?
   (b) What is an oxidising agent? Include an example in your answer.
4. Using solubility as an example, explain why an homologous series shows a trend in physical properties rather than each member of the series displaying the same property.
5. For all the homologous series studied so far, copy and complete the table to summarise the systematic and the common group name of each series.

Common group name	Systematic group name
Alkanes	
Alkenes	
Alcohols	
Carboxylic acids	
Esters	
Amines	
Amides	
Aldehydes	
Ketones	

6. Using purple potassium permanganate solution as an oxidising agent, explain how you could distinguish an aldehyde from a ketone.
7. Explain, using equations, why hex-3-ene will change bromine water from yellow-brown to colourless, while hexane will not.
8. Identify the series of organic compounds which is characterised by each of the following.
   (a) Decolourises bromine water in the dark.
   (b) Reacts with sodium hydrogen carbonate to produce carbon dioxide.
   (c) Reacts with sodium to produce hydrogen gas.
   (d) Can be oxidised to carboxylic acids.
   (e) Releases ammonia gas when heated with sodium hydroxide.

14 Redox Reactions and Organic Compounds

The **oxidation number** (state) of a carbon atom in a compound can vary depending on what is attached to it. The oxidation state of carbon can vary from −4 in CH_4, to +2 in CO and +4 in CO_2. (Remember the oxidation state of O is −2 and that of H is +1.)

When an organic compound is involved in a redox reaction, we need to work out which carbon atom has changed oxidation state and by how much. Each carbon atom is considered separately.

To find out if a carbon atom has undergone an oxidation or reduction reaction you look for changes in bonds attached to that carbon atom.

- A **carbon atom is reduced** if, after the reaction, it has more bonds to H atoms and/or fewer bonds to very electronegative atoms such as O, N, F, Cl, Br, I or S.
- A **carbon atom is oxidised** if, after the reaction, it has fewer attached H atoms and/or more bonds to more electronegative atoms.

For example, in Figure 14.1 oxidation and reduction reactions using cyclohexene are shown. The carbon atoms drawn in blue are reduced and those drawn in red are oxidised.

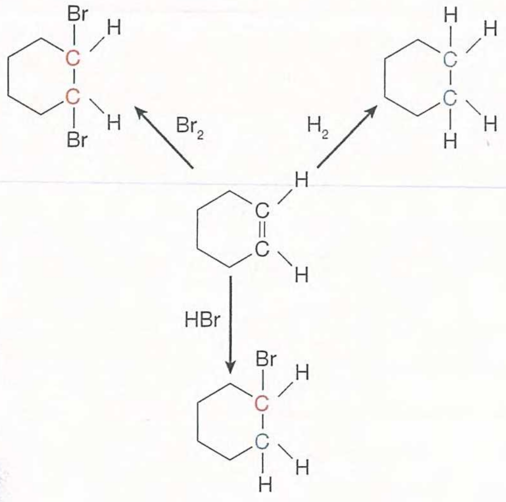


Figure 14.1 Redox reactions in cyclohexene.

In Figure 14.1 you can see the following reactions.

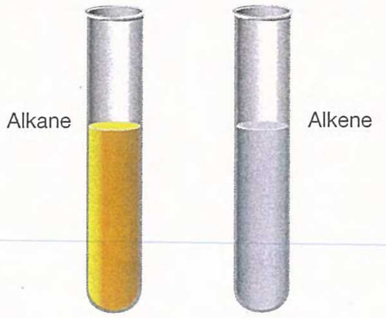
- Reaction with **bromine gas** (Br_2) causes an electronegative Br atom to be added to each carbon atom shown, so they are both **oxidised**. The oxidation number increases (from −1 to 0) as the bond to bromine is formed.
- Reaction with **hydrogen gas** (H_2) means an extra H atom is added to each C atom, so both C atoms are reduced. (The oxidation number decreases from −1 to −2 for both carbon atoms.)
- Reaction with **hydrogen bromide** (HBr) means that one C gains a H and is reduced – its oxidation number decreases (from −1 to −2), while the other C gains a Br atom and is oxidised – its oxidation number increases (from −1 to 0).

Distinguishing test for an alkene

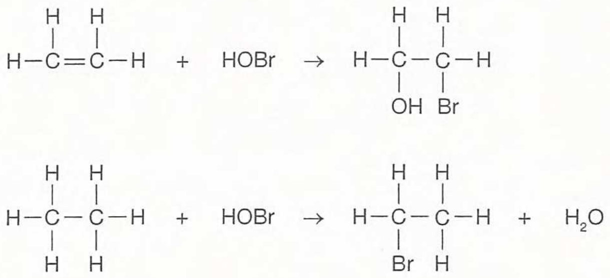
The test to **distinguish between an alkane and an alkene** is to add **bromine water**.

When you add bromine water (essentially BrOH) to a sample of each, the bromine water reacts very quickly with an **alkene**, rapidly changing from yellow-brown to colourless, even in the absence of light. The oxidation number of both carbon atoms has increased (from −2 to −1), indicating an **oxidation reaction.**

On the other hand, bromine water reacts only very slowly with an **alkane,** and only in the presence of ultraviolet light. So the bromine water remains a yellow-brown colour and only fades very slowly. Notice that in this case, the oxidation number only changes for the carbon which receives the Br atom. The other carbon atom is unchanged.



$$Br_2(l) + H_2O(l) \rightleftharpoons BrOH(aq) + H^+(aq) + Br^-(aq)$$



$$H_2C{=}CH_2 + HOBr \rightarrow H_2C(OH){-}CH_2Br$$

$$H_3C{-}CH_3 + HOBr \rightarrow H_3C{-}CH_2Br + H_2O$$

Figure 14.2 Bromine water on an alkane and an alkene.

Cyclohexene (C_6H_{10}) is frequently used to show the reduction of alkenes in laboratories because it is non-volatile and exists in liquid form at room temperature.

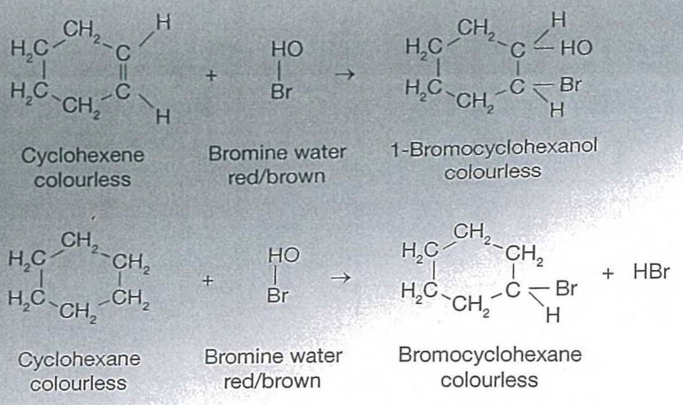


Figure 14.3 Cyclohexane, cyclohexene and bromine water.

Oxidation of alcohols

Primary and secondary alcohols react **with oxidising agents** such as acidified potassium permanganate ($KMnO_4$) and acidified potassium dichromate ($K_2Cr_2O_7$). (Acidified means that an acid such as dilute sulfuric acid is added.)

Dichromate ions ($Cr_2O_7^{2-}$) are orange. When reduced, they are converted to chromate ions (Cr^{3+}) which are green as shown in Figure 14.4.

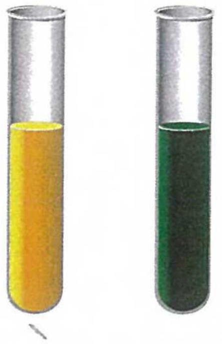
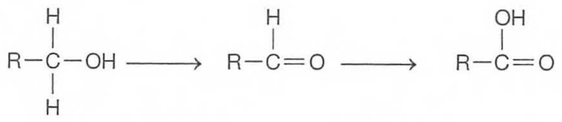


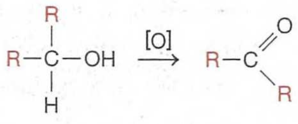
Figure 14.4 Reduction of dichromate to chromate ions.

Primary alcohols are oxidised to **aldehydes**, which can be further oxidised, under suitable conditions, to **carboxylic acids**.



Alcohol $\xrightarrow{\text{oxidation}}$ aldehyde $\xrightarrow{\text{oxidation}}$ carboxylic acid

- **Secondary alcohols** are oxidised to **ketones**, which do not get oxidised any further. Note that an [O] placed over an arrow is another way of indicating an oxidation reaction with an oxidising agent.



- **Tertiary alcohols** are not able to be oxidised.

Looking at Figure 14.5 might help you understand and remember these reactions. You can see that in primary and secondary alcohols the oxidising agent is removing a H from a C atom and from a hydroxyl group attached to that C. However, in tertiary alcohols, there is no H (attached to the C atom) to be removed – so no oxidation can occur.

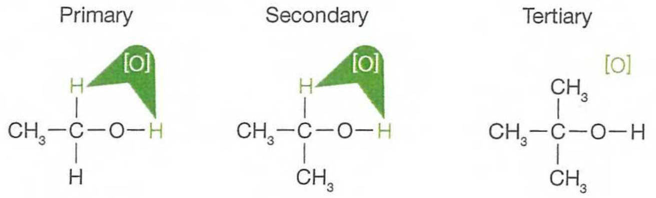
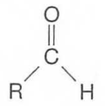


Figure 14.5 Oxidation of alcohols.

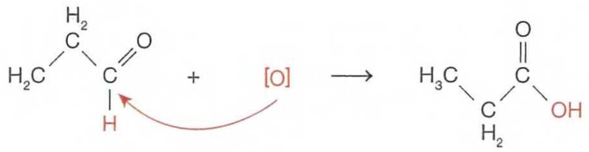
Oxidation of aldehydes

Aldehydes are oxidised to carboxylic acids. The presence of the H atom on the carbon with the =O attached makes aldehydes easy to oxidise as they become strong reducing agents.



For example:

Propanal $\xrightarrow{[O]}$ propanoic acid



Summary of organic reactions

Redox reactions involving organic compounds are summarised in Table 14.1.

Table 14.1 Redox reactions involving organic compounds.

Type of compound	Oxidation or reduction
Alkene C_nH_{2n}	Reduced to alkanes with hydrogen gas. Oxidised to alcohols by bromine water.
Alcohol $C_nH_{2n+1}OH$	Reduced to alkenes. Primary alcohols oxidised to aldehydes then to carboxylic acids. Secondary alcohols oxidised to ketones. Tertiary alcohol – not oxidised.
Aldehydes RCHO	Oxidised to carboxylic acids.
Amides R-$CONH_2$	Reduced to amines.