

Life on Earth is carbon based. This is because the structures of living things on Earth are based mainly on organic compounds whose structures have a carbon skeleton. The growth and decay of living things involve a series of reactions in which these organic compounds are made, decomposed or changed from one form to another.

For example, photosynthesis and respiration in plants are processes that involve organic reactions. Building muscle and other tissues, digesting food and the decay of dead organisms all involve reactions of organic compounds. Therefore, the reactions of organic compounds are vital to life.

The industrial production of many chemicals also involves organic reactions. These reactions include the manufacture of paints, plastics, pharmaceuticals and foods.

At the end of this chapter, you will be able to describe some specific chemical reactions involving organic compounds, including oxidation, addition and condensation reactions. You will learn that the functional groups of compounds are usually involved in chemical reactions and, thus, members of a homologous series usually undergo similar reactions because they have the same functional group.

Science understanding

- Organic molecules have a hydrocarbon skeleton and can contain functional groups, including alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides; functional groups are groups of atoms or bonds within molecules which are responsible for the molecule's characteristic chemical properties
- Functional groups within organic compounds display characteristic chemical properties and undergo specific reactions; these reactions include addition reactions of alkenes, redox reactions of alcohols, and acid–base reactions of carboxylic acids; these reactions can be used to identify the functional group present within the organic compound
- All alcohols can undergo complete combustion; with oxidising agents, including acidified MnO_4^- or $\text{Cr}_2\text{O}_7^{2-}$, oxidation of primary alcohols produces aldehydes and carboxylic acids, while the oxidation of secondary alcohols produces ketones; these reactions have characteristic observations and can be represented with equations
- Alcohols can react with carboxylic acids in a condensation reaction to produce esters and can be represented with equations

Science as a human endeavour

- Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts (green chemistry), including the production of ethanol and biodiesel

14.1 Chemical properties of alkenes



FIGURE 14.1.1 Vegetable oils are organic compounds that can be converted to margarine by reacting them with hydrogen gas.

The properties and reactions of an organic compound are largely determined by the functional groups in the compound. As all members of a homologous series have the same functional group, the members of that series typically undergo the same type of reactions.

For example, alkenes are a homologous series of compounds that contain a carbon–carbon double bond. Vegetable oils are liquids that contain alkene molecules that have one or more carbon–carbon double bonds. Vegetable oils react with hydrogen gas to form semisolid substances that have a consistency suitable for spreading on bread. These semisolid products (for example, margarine) provide an alternative to **saturated** fats such as those found in butter (Figure 14.1.1).

The production of margarine involves an addition reaction. In this section, you will learn about addition reactions and other typical reactions that alkenes undergo and the reaction conditions required.

REACTIONS OF ALKENES

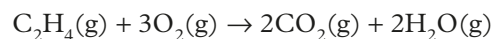
Alkenes and alkanes are hydrocarbons. Hydrocarbons are molecules that contain only the elements hydrogen and carbon. Alkenes are described as **unsaturated** hydrocarbons because they contain a carbon–carbon double bond. You studied the structure and naming of alkanes and alkenes in Year 11 Chemistry and in Chapter 13. Some examples are listed in the Table 14.1.1.

TABLE 14.1.1 Nomenclature and structures for some simple straight chain alkanes and alkenes

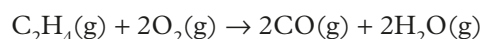
Alkane name	Formula	Structure	Alkene name	Formula	Structure
ethane	C ₂ H ₆	<pre> H H H—C—C—H H H</pre>	ethene	C ₂ H ₄	<pre> H H \ / C=C / \ H H</pre>
butane	C ₄ H ₁₀	<pre> H H H H H—C—C—C—C—H H H H H</pre>	but-2-ene	C ₄ H ₈	<pre> H C H \ / \ C=C C / \ / \ H C H H H H</pre>

Combustion in air

You have previously learnt that alkanes are rather unreactive, but burn in oxygen to produce carbon dioxide and water. This releases heat, thus making alkanes good fuels. Alkenes also burn in an excess of oxygen to produce carbon dioxide and water. The equation for the combustion of ethene is:



Note that in a limited supply of oxygen, incomplete combustion can occur and carbon monoxide is produced instead of carbon dioxide. The equation for the incomplete combustion of ethene is:



Addition reactions of alkenes

The carbon–carbon double bond in alkenes has a significant effect on the chemical properties of the homologous series. Alkenes are generally more reactive compounds than alkanes, which contain only single bonds. The reactions of alkenes usually involve addition of a small molecule across the double bond. These reactions are called **addition reactions** because two reactants combine (or add) to give a single product.

During addition reactions:

- two reactant molecules combine to form one product molecule
- the carbon–carbon double bond of the alkene becomes a single bond
- an unsaturated compound becomes saturated
- the atoms of the small molecule adding to the alkene are ‘added across the double bond’. The small molecule splits into two parts, which add to either end of the original double bond. This can be seen in the reaction of hydrogen bromide with ethene in Figure 14.1.2.

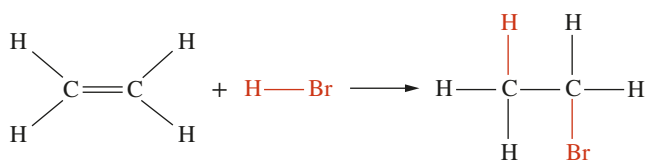


FIGURE 14.1.2 The reaction between ethene and hydrogen bromide. This is an example of an addition reaction between an alkene and a hydrogen halide.

When ethene reacts with hydrogen bromide, an addition reaction occurs and bromoethane is the only product. During this reaction, the hydrogen atom from the HBr molecule forms a covalent bond to one carbon atom in the double bond of ethene and the bromine atom forms a bond to the other carbon atom. Unlike substitution reactions (see Revision box), there is no **inorganic** product formed. All the atoms in the reactants end up in the final product.

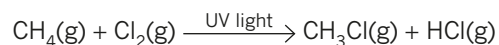
REVISION

Substitution reactions

In Year 11 Chemistry, you learnt that alkanes undergo a type of reaction called substitution. A **substitution reaction** occurs when an atom or functional group in a molecule is replaced or ‘substituted’ by another atom or group.

Alkanes undergo substitution reactions with halogens, such as chlorine and bromine, to produce haloalkanes. For the substitution reaction to occur, the reaction must be initiated by ultraviolet (UV) light.

The reaction between methane and chlorine in the presence of UV light is shown by the equation:



For each molecule of chlorine gas (Cl_2) that reacts, a hydrogen atom on the alkane is replaced by a chlorine atom.

There are four different types of addition reactions of alkenes that you need to learn about. These were all introduced in Year 11 Chemistry and are explained in detail below.

Reactions of alkenes with hydrogen

Alkenes react with hydrogen gas in the presence of a metal catalyst such as nickel to form alkanes. This reaction is known as a hydrogenation reaction and forms a saturated alkane. The reaction shown in Figure 14.1.3 is the hydrogenation of ethene with hydrogen gas to produce ethane.

The activation energy for this reaction is too high for the reaction to proceed at room temperature without a catalyst.

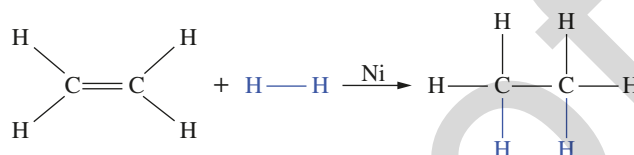


FIGURE 14.1.3 The addition reaction of ethene with hydrogen to form the saturated alkane, ethane. Note that nickel is used as a catalyst in this reaction.



FIGURE 14.1.5 (a) When an alkene is added to aqueous bromine, the alkene reacts with the coloured bromine and the solution loses colour. (b) When an alkane is added to aqueous bromine, no addition reaction occurs and so the colour remains.

Reactions of alkenes with halogens

Figure 14.1.4 shows the reaction of ethene with bromine to form 1,2-dibromoethane. The halogen adds across the double bond of the molecule, so in the product there is one bromine atom attached to each carbon atom.

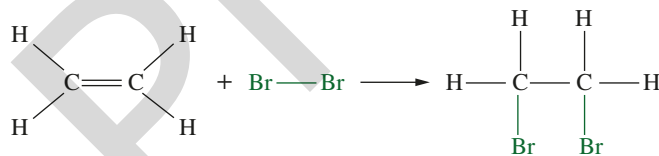


FIGURE 14.1.4 The addition reaction of ethene with bromine produces 1,2-dibromoethane.

This reaction proceeds at room temperature without a catalyst. Other halogens such as Cl_2 and I_2 also undergo addition reactions with alkenes to form the corresponding disubstituted haloalkanes.

Bromine is often used to test for the presence of a carbon-carbon double bond because of the ease and speed with which it reacts with an alkene. The orange colour of the bromine quickly disappears when it is mixed with an alkene (Figure 14.1.5).

Reactions of alkenes with hydrogen halides

Just as you saw with the reaction of ethene and hydrogen bromide, but-2-ene reacts with hydrogen chloride, a **hydrogen halide**, in an addition reaction. Figure 14.1.6 shows the reaction of but-2-ene with hydrogen chloride to produce a single product, 2-chlorobutane. In this reaction, a hydrogen atom adds to one of the carbon atoms in the carbon-carbon double bond and a halogen atom adds to the other carbon atom.

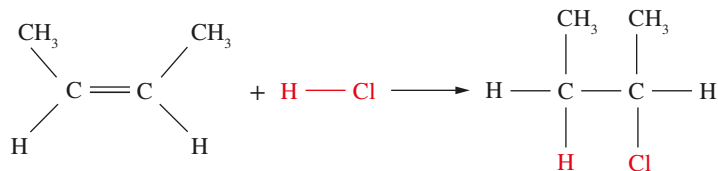


FIGURE 14.1.6 The addition reaction of but-2-ene with hydrogen chloride produces 2-chlorobutane.

However, as Figure 14.1.7 shows, when hydrogen chloride reacts with but-1-ene, two products are possible.

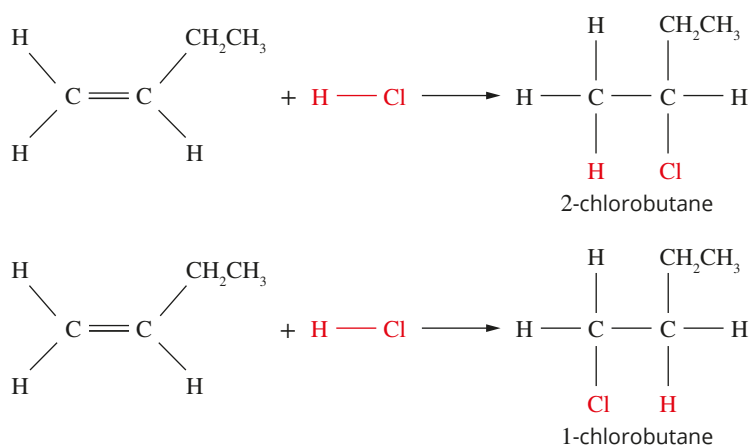


FIGURE 14.1.7 The addition reaction of but-1-ene with hydrogen chloride. Two isomers are possible as products.

The addition reaction can produce two isomers. In one product, the hydrogen atom from the hydrogen chloride molecule has been added to the carbon atom in the carbon-carbon double bond at the end of the but-1-ene molecule (C1). In the other product, the hydrogen atom has been added to a carbon atom at the other end of the carbon-carbon double bond (C2).

When you react an asymmetrical alkene with an asymmetrical reactant, as is the case in Figure 14.1.7, isomers are produced. More of one isomer is usually produced than the other because one of the reactions is more likely to occur than the other. The reasons for this depend on the ‘mechanism’ for the reaction, which is beyond the scope of Year 12 Chemistry.

Reactions of alkenes with water

Alkenes react with water under specific conditions to form the corresponding alcohol. For example, an addition reaction of ethene and water, using an inorganic acid catalyst, will produce ethanol. Figure 14.1.8 shows the addition reaction of steam and ethene, using a phosphoric acid catalyst. This reaction is used in industry for the production of ethanol.

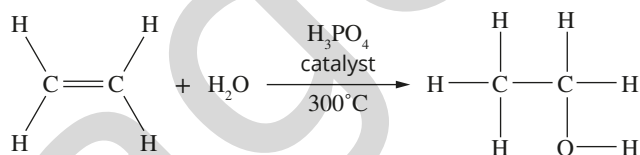


FIGURE 14.1.8 The addition reaction of ethene with water in the presence of a phosphoric acid catalyst produces ethanol.

The reaction is carried out at 300°C. The gaseous reactants are passed over a solid bed of the catalyst and gaseous ethanol is formed.

The reaction of ethene with steam is often described as a **hydration reaction**. Hydration reactions are reactions that involve water as a reactant. In the addition reaction, water is ‘added’ across the double bond. The reaction is used for the commercial manufacture of ethanol because it is a one-step process that uses little energy, apart from initial heating. The heterogeneous nature of the reaction system means it is easy for manufacturers to remove the product from the reaction mixture, leaving the catalyst intact.

i Reactions that involve water as a reactant are referred to as hydration reactions.

Addition polymerisation

Alkenes can also react with each other in addition reactions to form **polymers** (meaning 'many units'). The reaction of ethene with itself to form polyethene, shown in Figure 14.1.9, is an example of an **addition polymerisation** process. The small molecule that undergoes the addition reaction (ethene) is called a **monomer** ('one unit'). Several thousand ethene monomers usually react to make one molecule of polyethene. (Polymerisation is covered in more detail in Chapter 15.)

Other alkenes react in a similar way. For example, propene forms polypropene and butene forms polybutene.

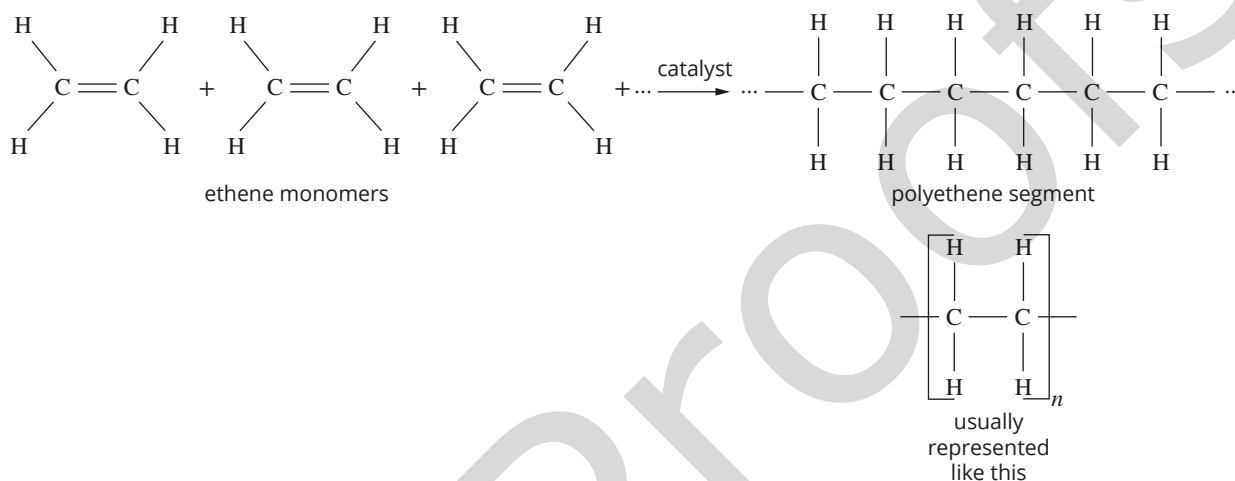


FIGURE 14.1.9 Thousands of ethene monomers join together in an addition reaction to make one chain of polyethene. The standard notation shown on the right simplifies the drawing of such a large chain.

CHEMFILE

Making margarine

The raw materials used to make many margarines include vegetable oils. Most vegetable oils are liquids and so cannot be spread on bread in the same way as butter.

Vegetable oils contain long hydrocarbon chains that are polyunsaturated; that is, they contain a number of carbon-carbon double bonds. If some of these double bonds are converted to single bonds, the molecules can pack more closely, resulting in stronger dispersion forces between the molecules and therefore higher melting points. The liquids become semisolids and the product is then suitable for spreading.

One of the steps in making margarine from a vegetable oil usually involves reacting vegetable oils with hydrogen gas, using a metal catalyst such as nickel. In this step, some of the carbon-carbon double bonds react with the hydrogen in an addition reaction, and are converted into single bonds, as shown in Figure 14.1.10.

Note that in this type of diagram the carbon and hydrogen atoms are not represented by letters. Each 'kink' in the long chains represents a carbon atom with two hydrogen atoms attached. Where a double bond is shown, each carbon atom in the double bond has only one hydrogen atom attached to it.

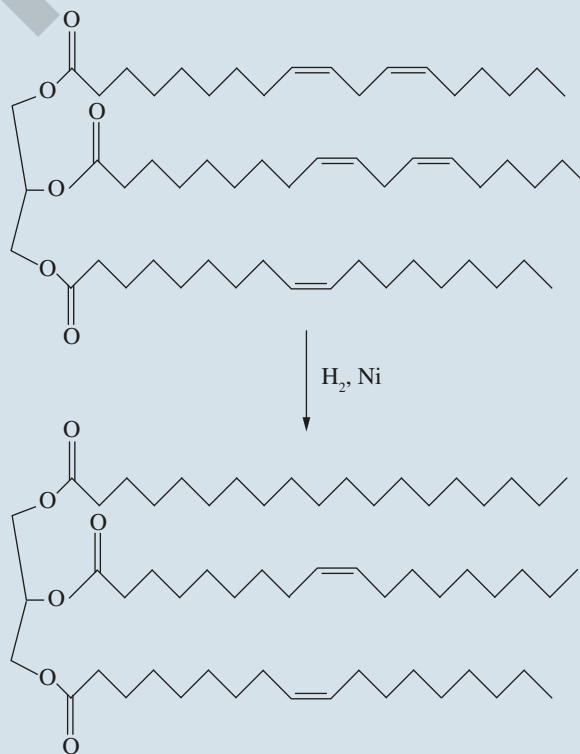


FIGURE 14.1.10 Hydrogenation of some of the carbon-carbon double bonds in a vegetable oil can convert it from a liquid into a 'spreadable' semisolid.

14.1 Review

SUMMARY

- Alkenes burn in the presence of oxygen to produce carbon dioxide and water.
- Alkenes are unsaturated hydrocarbons. They undergo addition reactions to produce saturated compounds.
- Alkenes undergo addition reactions with:
 - hydrogen and a metal catalyst to produce alkanes
 - halogens to produce dihaloalkanes
 - hydrogen halides to produce haloalkanes
 - water and an inorganic acid catalyst to produce alcohols.
- Alkenes undergo addition polymerisation reactions to form polymers containing only carbon-carbon single bonds.

KEY QUESTIONS

- Name the products formed when ethene reacts with:
 - hydrogen chloride
 - chlorine
 - water
 - hydrogen.
- Use structural formulas to write equations and name the products for the reactions of:
 - but-1-ene with chlorine
 - but-2-ene with hydrogen bromide.
- Name the organic products formed when each of the following pairs of compounds react.
 - Ethene and water in the presence of sulfuric acid
 - Hex-3-ene and hydrogen chloride
- Write equations for the production of:
 - propane from propene
 - 2,3-diiodobutane from but-2-ene
 - pentan-3-ol from pent-2-ene.
- Write the structural formula (showing all atoms and bonds) of the alkene that could be used to produce:
 - 2,3-dibromohexane
 - 3-chloropentane.

14.2 Chemical properties of alcohols



FIGURE 14.2.1 Ethanol (*álcool*) is used as a fuel in Brazil and is cheaper than petrol (*gasolina*), although petrol delivers better fuel consumption.

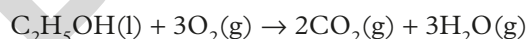
As you learnt in section 14.1, alcohols can be produced by addition reactions of alkenes. Ethanol is the most widely used alcohol in society. You may have seen E10 fuel being sold at your local service station. The E10 classification indicates that the petrol contains 10% ethanol. In Brazil, ethanol fuels are widely used, with the percentage of ethanol being a minimum of 20–25% (Figure 14.2.1). Some cars have been developed to run on 100% ethanol. The ethanol in Brazil is considered a renewable biofuel because it is sourced from the fermentation of sugar cane. The combustion of bioethanol for fuel was studied in Year 11 Chemistry and you will study the synthesis of biodiesel as a further example of a biofuel in Chapter 16.

The presence of the hydroxyl functional group means ethanol has very different properties from ethene or chloroethane. These properties make ethanol useful in a wide variety of applications. Ethanol is a liquid at room temperature and is highly soluble in water because of its ability to form hydrogen bonds. It is widely used as a solvent in cosmetics and pharmaceuticals, as well as in alcoholic drinks such as wine, beer and spirits. When consumed, ethanol acts as a depressant on the human body, slowing reactions and responses. Excess ethanol consumption also blocks the production of antidiuretic hormones, increasing urination and resulting in dehydration.

In this section, you will examine some of the common reactions that alcohols undergo.

COMBUSTION OF ALCOHOLS

Just like alkanes and alkenes, alcohols burn readily in air to form carbon dioxide and water as products. The equation for the combustion of ethanol is:



This is a highly exothermic reaction, so ethanol is used as a fuel. On a smaller scale, methylated spirits, which contains about 95% ethanol mixed with other chemicals, is used as a fuel for camping stoves. Some cooking techniques make use of the burning of alcohol for effect and flavour. Figure 14.2.2 shows how the ethanol in brandy can burn as it is added to enhance the flavour of a Christmas pudding.



FIGURE 14.2.2 Burning brandy is sometimes poured over a Christmas pudding to add flavour. Brandy can contain as much as 40% ethanol.

Oxidation of alcohols

The combustion of alcohols and other fuels can be classified as a type of oxidation–reduction (redox) reaction. Alcohols can also be oxidised by strong inorganic oxidising agents such as acidic solutions of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and potassium permanganate (KMnO_4). The products of these oxidation reactions depend on the type of alcohol involved.

Alcohols can be classified (see Chapter 13) into three types—primary, secondary or tertiary—depending on the position of the hydroxyl group within the molecule.

- **Primary alcohols** have the $-\text{OH}$ group bonded to a carbon that is attached to only one alkyl group. These alcohols first oxidise to form **aldehydes** and then further oxidation forms the corresponding carboxylic acids.
- **Secondary alcohols** have the $-\text{OH}$ group bonded to a carbon that is attached to two alkyl groups. These alcohols oxidise to form **ketones**.
- **Tertiary alcohols** have the $-\text{OH}$ group bonded to a carbon that is attached to three alkyl groups. These alcohols are not oxidised by the oxidising agents listed above.

You can see in Figure 14.2.3 how the different isomers of butanol can be classified as primary, secondary or tertiary alcohols. Chemists often use the symbols 1° , 2° and 3° as a shorthand way of indicating whether an alcohol is primary, secondary or tertiary, respectively.

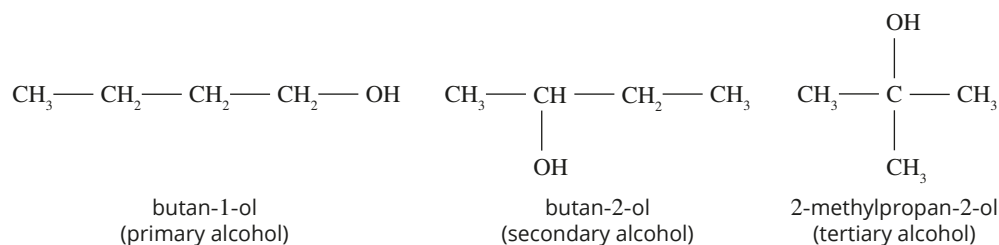


FIGURE 14.2.3 Structures of some primary, secondary and tertiary alcohols

Oxidation of primary alcohols

Figure 14.2.4 shows how a primary alcohol can be oxidised to a carboxylic acid in two stages.

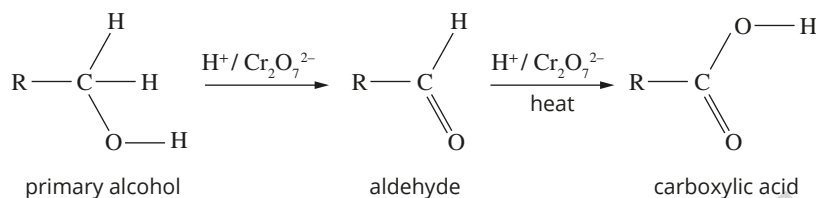


FIGURE 14.2.4 The general reaction for the oxidation of a primary alcohol

In the first stage, the primary alcohol is oxidised to an aldehyde. In the second stage, further heating of the reaction mixture in the presence of the oxidising agent oxidises the aldehyde to a carboxylic acid.

The example in Figure 14.2.5 shows that propan-1-ol is oxidised first to propanal (an aldehyde) and then to propanoic acid (a carboxylic acid).

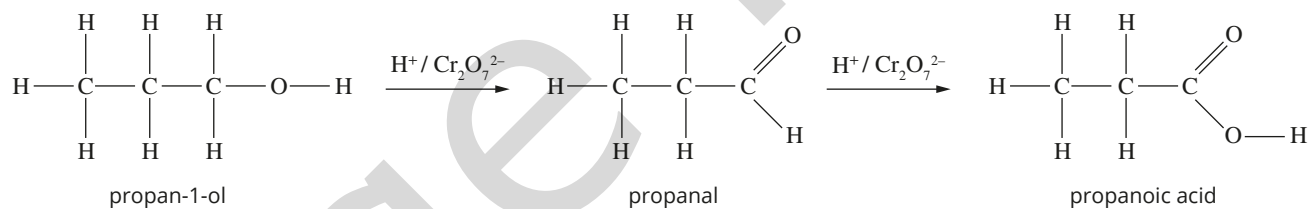


FIGURE 14.2.5 Reactions for the oxidation of the primary alcohol propan-1-ol

If the required product is an aldehyde, milder conditions (lower temperatures and shorter reaction times) must be used and the aldehyde can be distilled from the reaction mixture as it is formed so that it is not oxidised further. If the required product is the carboxylic acid, higher temperatures and longer reaction times are used.

i Aldehydes are produced as an intermediate in the oxidation of a primary alcohol to a carboxylic acid. If an aldehyde is the required product, it can be distilled off as it forms to prevent further oxidation.

Oxidation of secondary alcohols

When secondary alcohols are oxidised by strong oxidising agents, such as solutions of acidified potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) or potassium permanganate (KMnO_4), the corresponding ketones are produced. Figure 14.2.6 gives the general reaction for the oxidation of secondary alcohols to ketones.

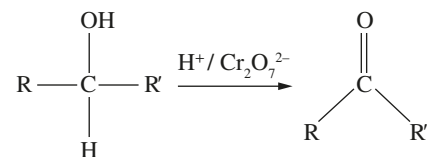


FIGURE 14.2.6 The general reaction for the oxidation of a secondary alcohol. The R groups in the structures represent different alkyl groups.

Figure 14.2.7 gives the equation to produce the ketone propanone by the oxidation of the secondary alcohol propan-2-ol. Propanone is commonly known as acetone and is a common solvent used in nail polish remover and glues.

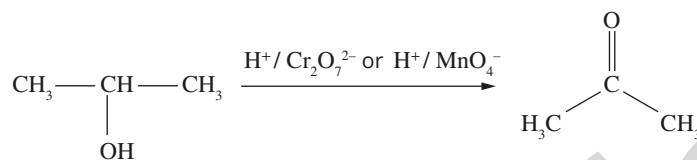


FIGURE 14.2.7 The secondary alcohol propan-2-ol can be oxidised to propanone.

i Tertiary alcohols are not normally oxidised by heating in the presence of a strong oxidant such as acidified dichromate or acidified permanganate.

Tertiary alcohols and oxidising agents

Tertiary alcohols are resistant to reaction with solutions of acidified potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) or potassium permanganate (KMnO_4).

During the oxidation of alcohols, there is an increase in the number of C–O bonds and a simultaneous decrease (at the same carbon atom) in the number of C–H bonds. In tertiary alcohols, the carbon attached to the hydroxyl group does not have a C–H bond to break, so oxidation cannot occur at that carbon atom.

Colour changes in oxidation reactions

The strong oxidising agents potassium dichromate and potassium permanganate are both highly coloured due to the presence of the transition metal elements chromium (Cr) and manganese (Mn).

A solution of dichromate ions in water is orange. When this acidified dichromate solution is used to oxidise a primary or secondary alcohol, the dichromate is reduced to the chromium ion (Cr^{3+}), which is green. This colour change from orange to green can be used as a qualitative test to indicate that oxidation of an organic compound has taken place. The colour changes observed for the reaction of primary, secondary and tertiary alcohols with potassium dichromate are shown in Figure 14.2.8.

The rate of reaction may also help to distinguish a primary alcohol from a secondary alcohol. A primary alcohol will usually react faster than a secondary alcohol of similar chain length.

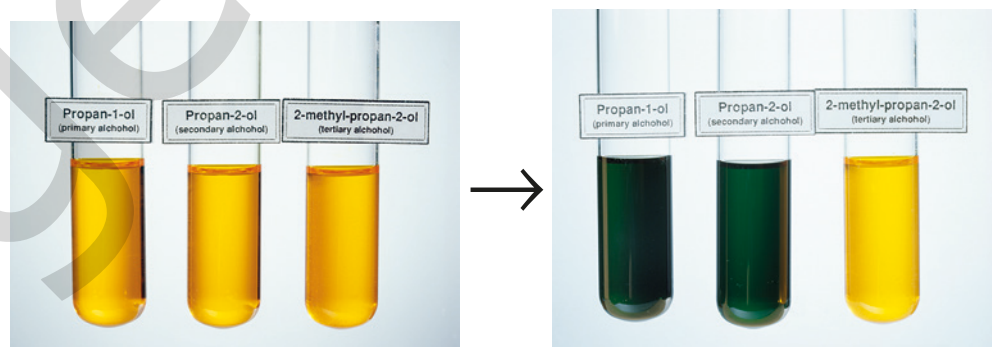


FIGURE 14.2.8 Solutions of the primary alcohol propan-1-ol and secondary alcohol propan-2-ol with acidified potassium dichromate change from orange to green on heating. Tertiary alcohols such as 2-methylpropan-2-ol will not react under these conditions so no colour change is observed.

A solution of acidified potassium permanganate is a deep purple colour. When this solution reacts with primary or secondary alcohols, the manganese in the permanganate ion (MnO_4^-) is reduced to Mn^{2+} , which is a very, very pale pink and appears colourless. Tertiary alcohols do not react so there is no change in the colour of the solution (Figure 14.2.9). As for the reaction with dichromate ions the rate of reaction of primary alcohols with permanganate ions is usually greater than it is for secondary alcohols.



FIGURE 14.2.9 The strong oxidising agent potassium permanganate is deep purple in colour. On reaction with primary and secondary alcohols, the colour changes from purple to colourless. The tertiary alcohol is resistant to oxidation under these conditions and does not react, so the solution does not change colour.

Table 14.2.1 summarises the reactions of primary, secondary and tertiary alcohols with an acidified solution containing dichromate or permanganate ions.

These reactions, and the associated colour changes can be used to determine whether a given alcohol is a primary, secondary and tertiary alcohol.

TABLE 14.2.1 Summary of the oxidation reactions of primary, secondary and tertiary alcohols with acidified dichromate solution or acidified permanganate solution

Type of alcohol	Oxidising agent	Products
Primary (1°)	Acidified dichromate solution or acidified permanganate solution	Aldehydes (under mild conditions) Carboxylic acids (at higher temperatures and longer reaction times)
Secondary (2°)	Acidified dichromate solution or acidified permanganate solution	Ketones
Tertiary (3°)	Acidified dichromate solution or acidified permanganate solution	No products because tertiary alcohols are resistant to oxidation by these oxidising agents

Writing equations for oxidation of alcohols

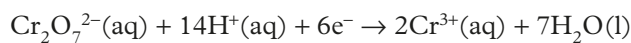
The reactions that take place when alcohols react with oxidising agents such as acidified dichromate or permanganate ions are redox reactions. To write balanced equations for the reactions, you write oxidation and reduction half-equations and combine them to construct overall equations for these reactions, as you learnt in Chapter 8.

For example, the oxidation of ethanol with acidified potassium dichromate can be represented by the following equations.

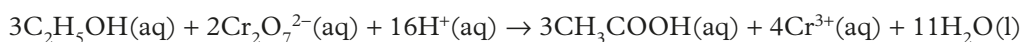
Oxidation half-equation:



Reduction half-equation:

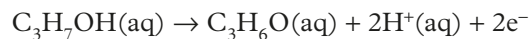


Overall equation:

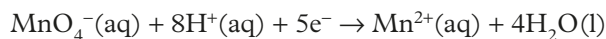


Another example is the oxidation of propan-1-ol with acidified potassium permanganate under mild conditions to give the aldehyde.

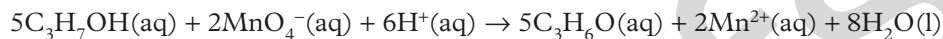
Oxidation half-equation:



Reduction half-equation:



Overall equation:



Worked example 14.2.1

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Propan-1-ol is oxidised to propanoic acid by acidified potassium permanganate. Write the half-equations for the reaction and hence write the balanced overall equation.	
Thinking	Working
Write the half-equation for the oxidation of the alcohol.	$\text{C}_3\text{H}_7\text{OH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_3\text{H}_6\text{O}_2(\text{aq}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$
Write the half-equation for the reduction of the oxidising agent. (This can normally be found in your Chemistry Data Booklet.)	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
Multiply one equation or both equations by a suitable factor to ensure that the number of electrons is balanced.	$5\text{C}_3\text{H}_7\text{OH}(\text{aq}) + 5\text{H}_2\text{O}(\text{l}) \rightarrow 5\text{C}_3\text{H}_6\text{O}(\text{aq}) + 20\text{H}^+(\text{aq}) + 20\text{e}^-$ $4\text{MnO}_4^-(\text{aq}) + 32\text{H}^+(\text{aq}) + 20\text{e}^- \rightarrow 4\text{Mn}^{2+}(\text{aq}) + 16\text{H}_2\text{O}(\text{l})$
Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Cancel out any species, such as H_2O or H^+ , that appear on both sides of the equation.	$5\text{C}_3\text{H}_7\text{OH}(\text{aq}) + 4\text{MnO}_4^-(\text{aq}) + 12\text{H}^+(\text{aq}) \rightarrow 5\text{C}_3\text{H}_6\text{O}(\text{aq}) + 4\text{Mn}^{2+}(\text{aq}) + 11\text{H}_2\text{O}(\text{l})$

Worked example: Try yourself 14.2.1

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Butan-1-ol is oxidised with acidified sodium dichromate under mild conditions to form butanal.

Write the half-equations for the reaction and hence write the balanced overall equation.

14.2 Review

SUMMARY

- Alcohols burn in the presence of oxygen to produce carbon dioxide and water.
- Alcohols react with oxidising agents, such as acidified solutions of dichromate ions and permanganate ions, in different ways.
 - Primary alcohols are oxidised first to aldehydes, which may be oxidised further to carboxylic acids.
 - Secondary alcohols are oxidised to ketones.
 - Tertiary alcohols are resistant to oxidation by these oxidising agents.
- Oxidation reactions can be used to identify the different types of alcohols.
- The different types of reactions you have studied in this module can be represented by chemical equations.

KEY QUESTIONS

- Pentan-3-ol, 2-methylbutan-2-ol and pentan-1-ol are all isomers of $C_5H_{12}O$.
 - Write an equation for the complete combustion of $C_5H_{12}O$.
 - Identify each isomer as a primary, secondary or tertiary alcohol.
 - For each isomer, show the reaction (using structural formulas—no balanced equations required) for all the reactions that would occur if the alcohol was heated with acidified potassium permanganate solution. Describe any colour changes that would be observed.
 - Give the name and structural formula for the alcohols that would produce the following products when oxidised with acidified dichromate.
 - Butanal
 - 3-Hexanone
- c**
-
- d**
-

14.3 Chemical properties of carboxylic acids



FIGURE 14.3.1 The ripening of blackberries involves many chemical reactions, including the conversion of carboxylic acids to esters.

Molecules that contain the carboxylic acid functional group are common in the natural world and are present in most plants. The sour taste of vinegar, lemons, yoghurt, rhubarb and most unripe fruits is due to the presence of carboxylic acids.

When fruits and berries like the blackberries in Figure 14.3.1 ripen, complex reactions take place. These include the conversion of carboxylic acids to other compounds. In some of these reactions, carboxylic acids react with alcohol molecules to produce esters. Esters give many fruits their characteristic aromas and tastes.

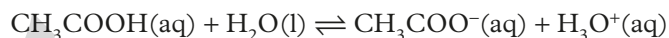
IONISATION IN WATER

You will remember from Chapter 4 that ethanoic (acetic) acid is a weak acid and only ionises to a small extent in water to form hydronium ions. Most carboxylic acids are weak acids and react with water in a similar way (Table 14.3.1).

TABLE 14.3.1 Acid ionisation constants (equilibrium constants) for two common inorganic acids and two common carboxylic acids

Acid	Formula	K_a at 25°C
Nitric acid	HNO_3	2.4×10^1
Hydrochloric acid	HCl	1.3×10^6
Ethanoic acid	CH_3COOH	1.8×10^{-5}
Methanoic acid	HCOOH	1.8×10^{-4}

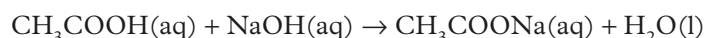
The reaction of a carboxylic acid with water is a reversible process so the equation for ionisation is written using equilibrium arrows. The equation for the ionisation of ethanoic acid in water is:



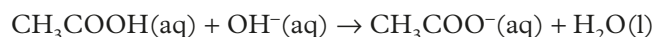
REACTIONS OF CARBOXYLIC ACIDS WITH METALS AND THEIR COMPOUNDS

Carboxylic acids undergo reactions typical of other acids, such as inorganic acids. Some examples are given below.

- Carboxylic acids react with metal oxides and hydroxides to give metal salts and water. For example, ethanoic (acetic) acid reacts with sodium hydroxide to produce sodium ethanoate (acetate) (the salt) and water. Note that when writing the formula of a salt of an organic acid, the formula of the metal ion is usually placed after the formula of the acid ion.

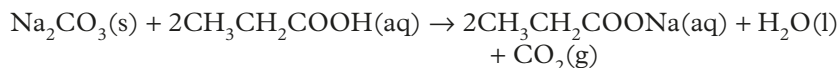


When writing these as ionic equations, the carboxylic acid is shown in its molecular form because most of the molecules are not ionised in the original solution:

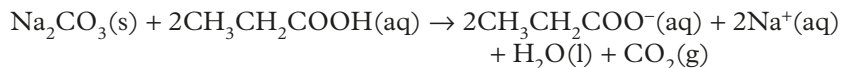


i The partial ionisation of carboxylic acids is because the equilibrium position of the reaction favours the reactants.

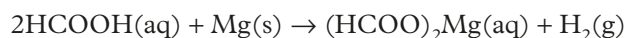
- Carboxylic acids react with metal carbonates and hydrogencarbonates to give a salt, water and carbon dioxide. For example, propanoic acid reacts with solid sodium carbonate:



Or ionic equation:



- Carboxylic acids react with reactive metals, such as sodium and magnesium, to give a salt and hydrogen gas. For example, methanoic acid reacts with magnesium:



Or ionic equation:



REACTIONS OF CARBOXYLIC ACIDS WITH ALCOHOLS

Reactions that involve the combination of two reactants and the elimination of a small molecule, such as water, are called **condensation reactions**. Esters are made by a condensation reaction between a carboxylic acid and an alcohol. A condensation reaction in which an ester is formed is also known as an **esterification reaction**.

For example, the ester ethyl ethanoate can be produced by gently heating a mixture of ethanol and pure ethanoic acid with a trace amount of sulfuric acid. The sulfuric acid acts as a catalyst. As well as the desired ester, water is produced.

The general equation for the esterification reaction involving a carboxylic acid and an alcohol is shown in Figure 14.3.3. Two examples of esterification reactions are also shown.

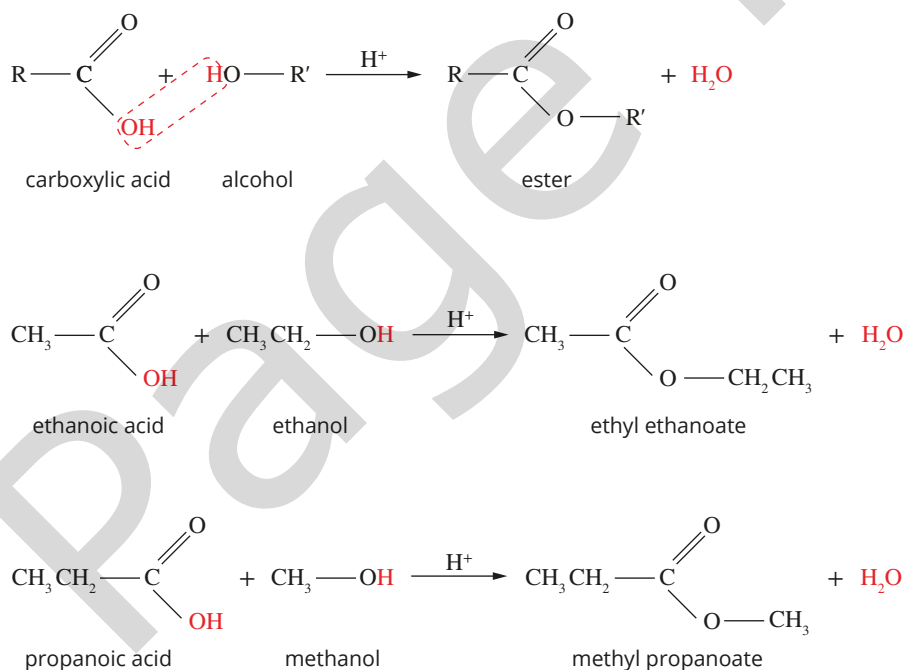


FIGURE 14.3.3 Esterification reactions occur when alcohols are heated with carboxylic acids and a small amount of sulfuric acid as a catalyst. The top reaction shows the general equation for esterification. Two specific examples are also shown: ethanoic acid with ethanol and propanoic acid with methanol.

CHEMFILE

Effervescence from a carboxylic acid reaction

The effervescence (bubbling) that occurs when some simple over-the-counter pain relievers or antacids are added to water is usually produced by the reaction of a carboxylic acid with a carbonate or hydrogencarbonate. Two common ingredients you may see listed on the packs of such medications are mineral salt 500 and food acid 334. Mineral salt 500 is the food additive code for sodium carbonate (or sodium hydrogencarbonate). Food acid 334 is the code for tartaric acid, commonly known as cream of tartar. Tartaric acid is a diprotic carboxylic acid (Figure 14.3.2). When placed in water these ingredients react with each other to release carbon dioxide gas which is the effervescence seen.

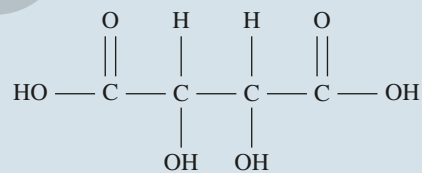


FIGURE 14.3.2 The structure of tartaric acid (IUPAC name 2,3-dihydroxybutanedioic acid). In water, tartaric acid ionises to produce hydronium ions, which can react with carbonates to produce carbon dioxide gas.

In the esterification reaction, it is the hydrogen atom from the hydroxyl group of the alcohol and the $-OH$ group from the carboxylic acid that combine to form water, which is the molecule eliminated in this condensation reaction.

As you learnt in Chapter 13, the first part of the name of an ester is derived from the name of the alcohol from which it was made. The second part of the name is derived from the name of the carboxylic acid from which it was made. Therefore, the name of the ester formed from methanol (an alcohol) and propanoic acid (a carboxylic acid) is methyl propanoate.

CHEMISTRY IN ACTION

Aspirin, an ester derived from a herbal remedy

Pharmaceutical products are often developed from substances found in plants that have been used as a traditional medicine. For example, the mild painkiller aspirin originated from a naturally occurring substance called salicin, which is found in the leaves and bark of willow trees and in the herb meadowsweet.

As long ago as 400 BCE, the Greek physician Hippocrates (Figure 14.3.4) recommended an infusion of willow leaves and bark to assist in childbirth and relieve other pains. It wasn't until 1829 that the active ingredient, salicin, was identified and isolated.

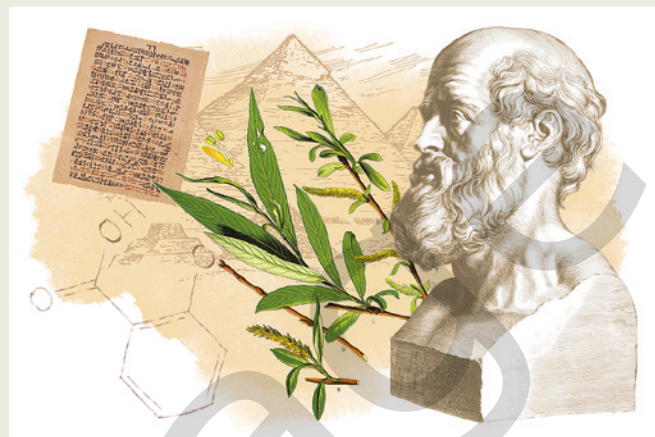


FIGURE 14.3.4 In 3000–1500 BCE, willow was used as a medicine by ancient civilisations such as the Sumerians and Egyptians. In Greece, in about 400 BCE, Hippocrates administered willow leaf tea to people suffering pain.

It is now known that the body converts salicin to salicylic acid, which is the active substance that helps to reduce fever and acts as a painkiller. Pure salicylic acid is hard to ingest and causes stomach irritation.

In 1897, Felix Hoffmann replaced the hydroxyl functional group on salicylic acid with an ester functional group to form acetylsalicylic acid, later named aspirin, which was much gentler on the mouth and stomach than salicylic acid.

The preparation of aspirin is a relatively simple process, involving one main step in which the hydroxyl functional group of a salicylic acid molecule reacts with the carboxylic acid functional group of an ethanoic acid molecule in a condensation reaction (Figure 14.3.5). The product, aspirin, has properties that are quite different from those of either of the two reactant molecules.

Although this reaction can be easily carried out in a laboratory, the yield is quite low. A more complex reaction is used to produce aspirin on an industrial scale.

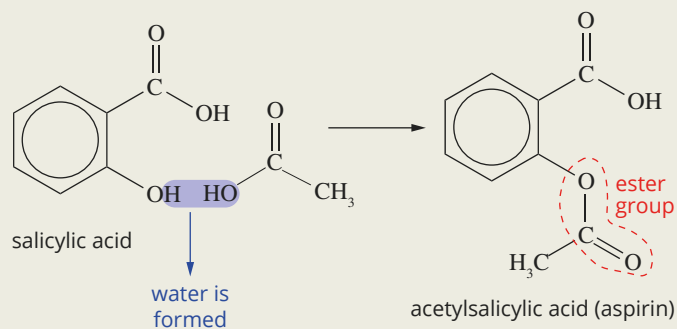


FIGURE 14.3.5 Aspirin can be made from salicylic acid and ethanoic acid. The process involves a reaction between hydroxyl and carboxyl functional groups to form an ester.

HYDROLYSIS OF ESTERS

The condensation reaction between carboxylic acids and alcohols is a reversible reaction. You can see in Figure 14.3.6 that esters can react with water to form a carboxylic acid and an alcohol. Reactions of this type are described as **hydrolytic reactions**, or simply **hydrolysis**. In effect, hydrolysis can be seen as the reverse of the condensation reaction used to produce the ester molecule. This reaction is catalysed by an alkali or dilute acid.

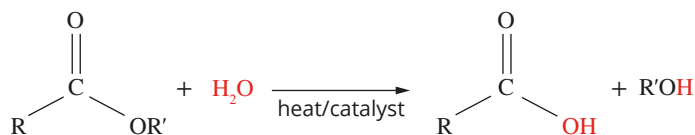


FIGURE 14.3.6 General equation for the hydrolysis of an ester: esters react with water to produce a carboxylic acid and an alcohol.

Figure 14.3.7 shows the equation for the hydrolysis of ethyl propanoate to form ethanol and propanoic acid using an acid catalyst.

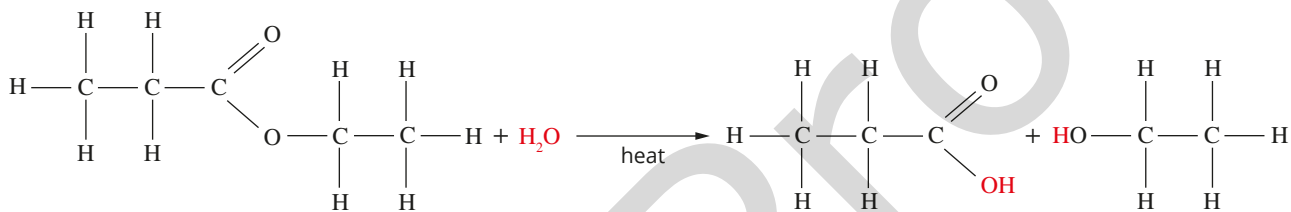


FIGURE 14.3.7 Equation for the acid-catalysed hydrolysis of ethyl propanoate to produce propanoic acid and ethanol.

When the hydrolysis of an ester is catalysed by an alkali such as sodium hydroxide, the products are an alcohol and the sodium salt of the carboxylic acid. The sodium salt can be easily converted to the carboxylic acid by adding dilute acid solution, such as hydrochloric acid.

The hydrolysis of esters by alkalis to produce soaps will be studied in Chapter 16.

i The hydrolysis of esters by metal hydroxides forms a salt of the carboxylic acid. Addition of excess acid regenerates the carboxylic acid.

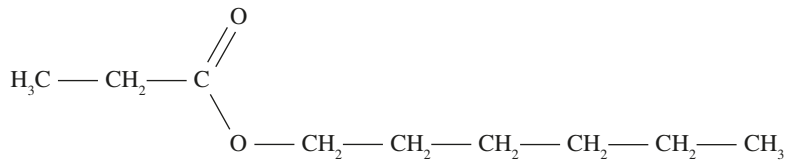
14.3 Review

SUMMARY

- Carboxylic acids are weak acids that ionise in water to produce hydronium ions and carboxylate ions.
- Carboxylic acids, like other acids, will react with:
 - reactive metals to produce a salt and hydrogen gas
 - metal oxides and hydroxides to produce a salt and water
 - metal carbonates and hydrogencarbonates to produce a salt, water and carbon dioxide.
- Carboxylic acids undergo condensation reactions with alcohols in the presence of an acid catalyst to produce esters.
- The condensation reaction to form an ester is called an esterification reaction.
- Esters can be hydrolysed by acids or alkalis to produce alcohols and carboxylic acids or their sodium salts, respectively.
- Each of the different types of reactions you have studied in this section can be represented by chemical equations.

KEY QUESTIONS

- Write the equation for the reaction that occurs when butanoic acid is added to water.
 - List the species (molecules and ions) present in the solution formed in part **a** from most to least abundant. Give a reason for the order of abundance.
- Give the formula and name for the conjugate base of propanoic acid.
- Write the ionic equations for the reactions that occur when the following are mixed:
 - aqueous solutions of ethanoic acid and potassium hydrogencarbonate
 - sodium metal and aqueous propanoic acid.
- Which one of the following combinations of reactants would not produce magnesium methanoate as a product?
 - Methanoic acid and magnesium chloride
 - Methanoic acid and magnesium hydroxide
 - Methanoic acid and magnesium metal
 - Methanoic acid and magnesium carbonate
- Write the equation for the reaction that occurs when methanoic acid and propan-1-ol are mixed in the presence of a small amount of sulfuric acid. Name the organic product.
- Name the reactants that would produce the following esters (assume no branching of carbon chains within the esters).
 - Pentyl ethanoate
 - Ethyl octanoate
 -



- $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_3$

14.4 Creating molecules: an introduction to organic synthesis

Organic chemists are highly skilled at developing compounds that have exactly the right properties needed for a particular purpose. These may be new pharmaceuticals, polymers or nano-materials. Once the desired compound has been identified, chemists must devise a way to make it. Chemists have to design an efficient method for converting readily available starting materials into the more complex product they want.

When selecting a chemical synthesis pathway, chemists need to consider the yield and purity of the products and also should minimise unwanted side-products and waste materials. Time and cost factors also need to be considered.

Modern chemists are also interested in devising environmentally sustainable synthetic routes. These pathways are designed to minimise waste, use 'greener' solvents, require less energy, and help to preserve the world's resources. This idea is discussed in more depth in Chapter 12.

In this section, you will learn how to devise **reaction pathways** for the synthesis of some simple organic compounds by utilising the reactions you have learnt about in sections 14.2 and 14.3.

SIMPLE REACTION PATHWAYS

Figure 14.4.1 shows chemical reaction pathways that can be used to form some compounds from ethane or ethene. A reaction pathway is a series of one or more steps, or reactions, that can be used to convert a reactant containing certain functional groups to a desired product with different functional groups. The same inorganic reactants and reaction conditions can be applied to different hydrocarbon starting points to produce the same functional groups on the product molecules.

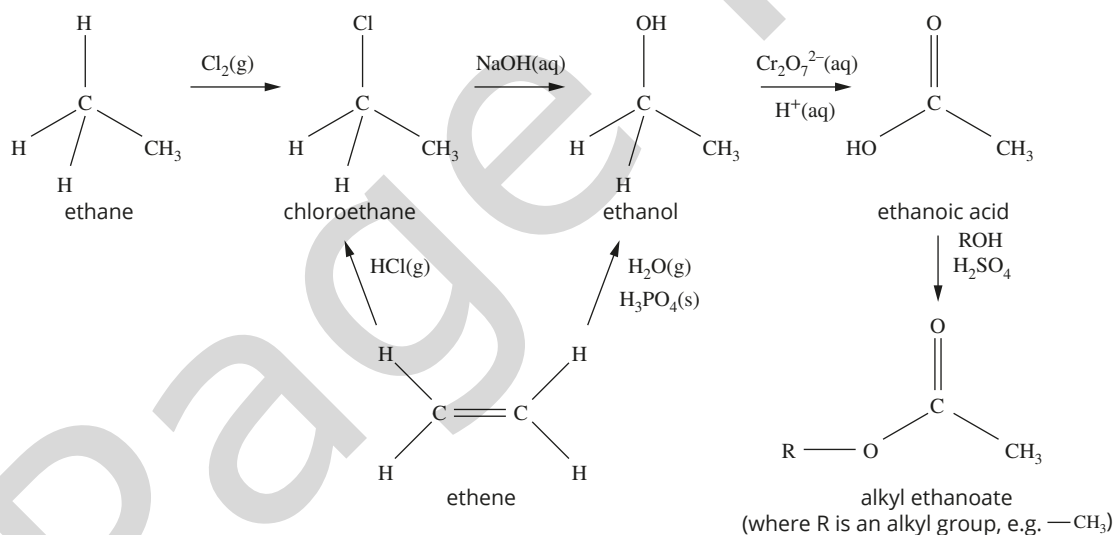


FIGURE 14.4.1 Some reaction pathways based on ethane and ethene. The same reaction conditions can be used to develop pathways for other members of the alkane and alkene homologous series.

CHEMFILE

Building the impossible

The chemist Robert Burns Woodward (Figure 14.4.2) was awarded the 1965 Nobel Prize in Chemistry for his synthesis of complex organic molecules. He devised procedures to synthesise complex natural products considered impossible to replicate in the laboratory. His approach resulted in the development of several rules still used by organic chemists to plan and predict how reactions will occur to devise sequential pathways to synthesise complex molecules.

When awarded the Nobel Prize, Woodward had synthesised large complex molecules such as quinine, cholesterol, cortisone, strychnine, reserpine and chlorophyll. His work on vitamin B₁₂, a large molecule (Figure 14.4.3), is considered to be the most complex. The synthesis took 69 steps and more than 12 years with the combined efforts of over 100 people from around the world.

The discoveries made during the synthesis of vitamin B₁₂ have contributed greatly to organic chemistry and were recognised with another Nobel Prize, in 1981. The prize was awarded to Roald Hoffmann, who worked with Woodward on the synthesis, and Kenichi Fukui, who had devised an alternative approach with a similar result to Hoffman and Woodward. Woodward died in 1979, and because Nobel Prizes are not awarded posthumously (after death), he was not named on the 1981 Nobel Prize.



FIGURE 14.4.2 Professor Robert Burns Woodward (1917–1979) synthesised complex organic molecules.

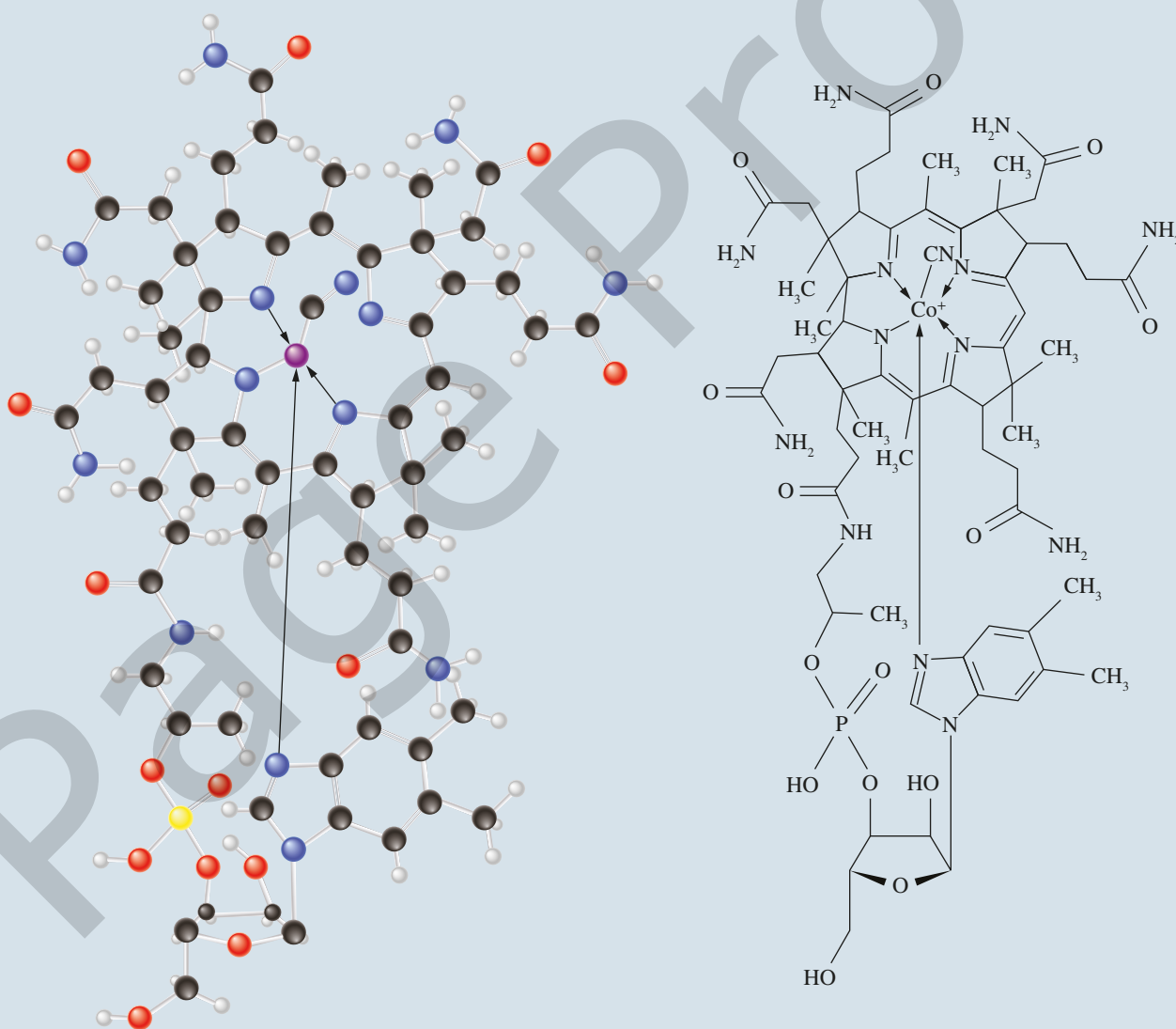


FIGURE 14.4.3 The structure of vitamin B₁₂. The manipulation of the functional groups and reaction conditions required to synthesise this large molecule from small starting materials takes 69 steps.

REACTION SEQUENCES: PRODUCTION OF ETHYL ETHANOATE

Ethyl ethanoate is an ester that has a wide range of uses. It is used as artificial fruit essences and flavours, and as a solvent in the decaffeination of tea and coffee. It is also used in the manufacture of printing inks and perfumes.

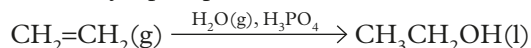
A close look at the structure of ethyl ethanoate (Figure 14.4.4) indicates that it is an ester and so can be produced by the condensation reaction between the appropriate carboxylic acid and alcohol—in this case, ethanoic acid and ethanol. Therefore, to synthesise ethyl ethanoate, you must first obtain ethanoic acid and ethanol.

Ethanol is an alcohol containing two carbon atoms. Ethanol can be synthesised from ethene by an addition reaction with water or by fermentation of sugars by yeasts. Ethene is a good choice for a starting material because it is readily available through the cracking of hydrocarbon fractions obtained from the distillation of natural gas and oil. The annual world production of ethene is 156 million tonnes.

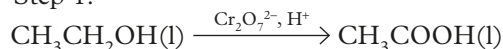
Ethanoic acid can then be made by oxidising some of the ethanol.

The manufacture of ethyl ethanoate is achieved in three steps.

Step 1: Ethanol is synthesised directly by the hydration of ethene in the presence of the catalyst phosphoric acid:



Step 2: Ethanoic acid is synthesised by oxidising some of the ethanol produced in Step 1:



Step 3: Ethyl ethanoate is produced by the condensation reaction between ethanoic acid and ethanol in the presence of sulfuric acid catalyst:

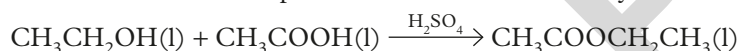


Figure 14.4.5 shows this chemical reaction pathway using structural formulas.

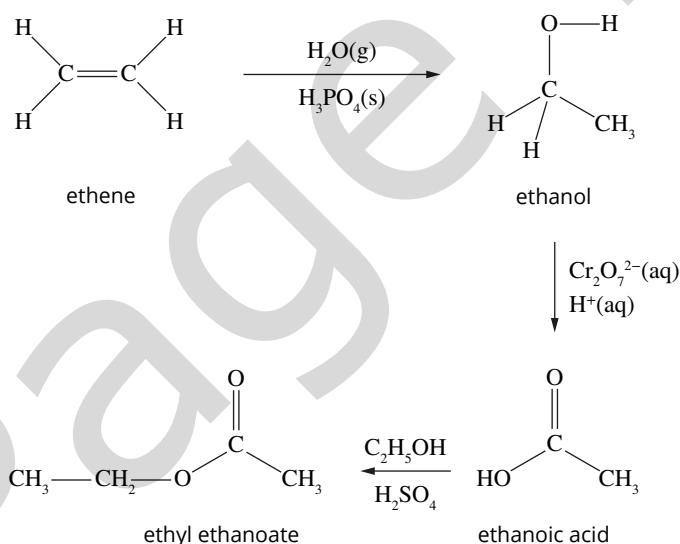


FIGURE 14.4.5 Synthetic pathway for the formation of ethyl ethanoate from ethene.

Considerations in devising a synthesis

As you saw in the synthesis of ethyl ethanoate, chemical synthesis pathways may require the preparation of several intermediate compounds. Some desired products can be synthesised by a number of routes so different possible pathways may also need to be considered. Chemists also consider issues such as yield, rate, cost, safety and sustainability when deciding on the preferred pathway.

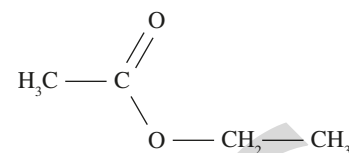
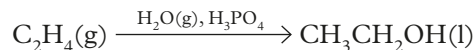


FIGURE 14.4.4 The ester ethyl ethanoate can be made by condensation of ethanoic acid with ethanol.

The methods of separation of the intermediate and final product from by-products must also be determined. The final product then needs to be purified and the purity evaluated.

Chemists must consider the yield of the product because not all of the reactants are necessarily converted to product. For example, in the reaction:



you would expect 100 kg of ethene to produce 164 kg of ethanol if all the ethene was converted to ethanol. If only 82 kg of ethanol was obtained, then the reaction yield would be 50%. Yields were discussed in more detail in Chapters 2 and 11.

Worked example 14.4.1

DESIGNING A CHEMICAL SYNTHESIS PATHWAY FOR AN ESTER

Design a reaction pathway for the synthesis of ethyl propanoate, starting with propan-1-ol and ethene.	
Thinking	Working
Write the structure of the ester to help determine which carboxylic acid and alcohol are required.	$\begin{array}{ccccccc} & \text{H} & \text{H} & \text{O} & & \text{H} & \text{H} \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{O} & - \text{C} & - \text{C} & - \text{H} \\ & & & & & & \\ & \text{H} & \text{H} & & & \text{H} & \text{H} \end{array}$ <p>The name ethyl propanoate indicates this is an ester. It is formed by a condensation reaction between an alcohol and a carboxylic acid. The first part of the name, 'ethyl', indicates the alcohol that reacted (ethanol) and the second part of the name, 'propanoate', indicates the carboxylic acid (propanoic acid).</p>
Write an equation for the reaction that forms the ester from the alcohol and carboxylic acid identified above.	$\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$
Identify the reactions that will produce each of the two reactants in the step above. (Continue these steps if necessary until all the chemicals required have been made from the starting compounds.)	<p>Propanoic acid is made by the oxidation of propan-1-ol:</p> $\begin{array}{ccccccc} & \text{H} & \text{H} & \text{O} & & \text{H} & \text{H} \\ & & & & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{O} & - \text{C} & - \text{C} & - \text{H} \\ & & & & & & \\ & \text{H} & \text{H} & & & \text{H} & \text{H} \end{array}$ <p>Ethanol is made by the hydration of ethene:</p> $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array} \xrightarrow[\text{H}_3\text{PO}_4]{\text{H}_2\text{O}} \begin{array}{ccccccc} & \text{H} & & \text{H} & & & \\ & & & & & & \\ \text{H} & - \text{C} & - & \text{C} & - \text{O} & - & \text{H} \\ & & & & & & \\ & \text{H} & & \text{H} & & & \end{array}$

Worked example: Try yourself 14.4.1

DESIGNING A CHEMICAL SYNTHESIS PATHWAY FOR AN ESTER

Design a reaction pathway for the synthesis of methyl ethanoate, starting with ethene and methanol.

CHEMISTRY IN ACTION

Keeping it moving forward

When chemical engineers design a synthesis, one of their aims is to maximise the yield of the desired product. For a synthesis where the reaction is reversible, an equilibrium may form and so limit yield. An equilibrium can only establish in a closed system, so chemical engineers design processes that do not occur in closed vessels. One approach is to continuously feed reactants into the reaction vessel in order to keep their concentrations high and so favour the forward reaction. Another approach is to remove products as they form to prevent the reverse reaction from occurring. Ideally, both these approaches are used at the same time.

The reaction of ethanoic acid with ethanol to form ethyl ethanoate is reversible. To maximise the yield of ethyl ethanoate, chemical engineers take advantage of the differences in boiling points of the substances involved.

The reaction mixture contains ethanoic acid, ethanol, ethyl ethanoate and water, which boil at 118°C, 78°C, 77.1°C and 100°C, respectively. As the reaction proceeds, ethyl ethanoate is removed from the reaction vessel by distillation (studied in Year 11 Chemistry). Although ethyl ethanoate has the lowest boiling point, distillation does not remove only ethyl ethanoate. At about 70°C, a mixture containing about 83% ethyl ethanoate, 8% water and 9% ethanol distills from the reaction mixture. Because about 10 times more ethyl ethanoate than ethanol is removed, the forward reaction is still favoured. Ethanoic acid has a higher boiling point (because it has dipole-dipole and hydrogen bonding in addition to dispersion forces) so it does not distill over.

As well, to further favour the forward reaction, the ratio of ethanoic acid to ethanol is kept high. This results in more ethanol reacting and less being available to distill

over with the ethyl ethanoate and water. Figure 14.4.6 shows the laboratory apparatus for a fractional distillation of a mixture of liquids.



FIGURE 14.4.6 Fractional distillation using a Liebig condenser (diagonal, centre) to separate a liquid into its component parts

14.4 Review

SUMMARY

- A reaction pathway is a sequence of more than one reaction that is used to convert a reactant into a product.
- Reaction pathways can be constructed from the organic reactions studied in this chapter.
- Reaction pathways indicate the reaction conditions and reagents required for each step.
- For maximum efficiency and profit, the production of an industrial chemical should occur at a fast rate with a high equilibrium yield.

KEY QUESTIONS

- 1 Devise reaction pathways for the following reactions.
 - a Butanoic acid from butan-1-ol
 - b Pentan-2-one from pent-1-ene
- 2 Propose the shortest reaction pathway that will synthesise:
 - a ethanol from ethene
 - b propyl methanoate from propan-1-ol and methanol.
- 3 Describe a reaction pathway to synthesise ethyl ethanoate from ethene.
- 4 In the production of ethanol by the addition reaction between ethene and water (in the form of steam), the ethene and steam are continuously fed into the reaction vessel. Explain how this improves the yield of ethanol.

Chapter review

KEY TERMS

addition polymerisation
addition reaction
aldehyde
condensation reaction
esterification reaction
hydration reaction
hydrogen halide

hydrolysis
hydrolytic reaction
inorganic
ketone
monomer
polymer
primary alcohol

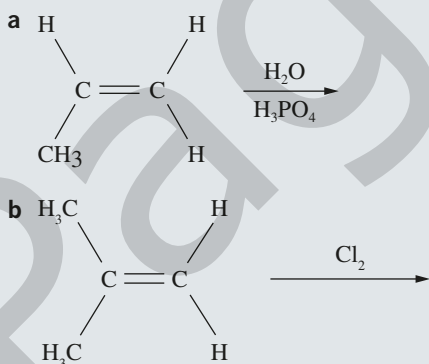
reaction pathway
saturated
secondary alcohol
substitution reaction
tertiary alcohol
unsaturated

Chemical properties of alkenes

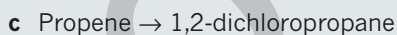
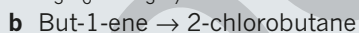
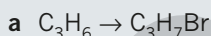
- 1 Complete this table about the different types of reactions of alkenes.

Reactants	Type of reaction	Product(s)
Alkene and hydrogen		
Alkene and hydrogen bromide		
Alkene and water (with a catalyst and heat)		
Alkene and bromine		
Alkene in the presence of a catalyst		

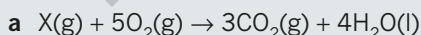
- 2 Write the structural formulas of the products of the following reactions.



- 3 Give the names of the chemicals, including any catalysts, that would be used to achieve the following conversions.

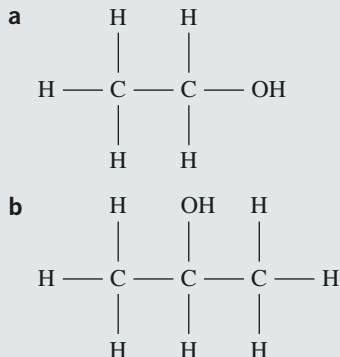


- 4 Alkanes, alkenes and alcohols all burn in air to form carbon dioxide and water. Equations for such a reaction are shown below. For each reaction, determine the formula of X, give its name and identify it is an alkane, alkene or alcohol.

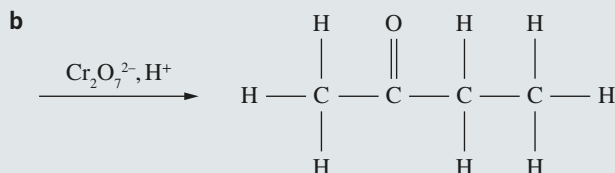
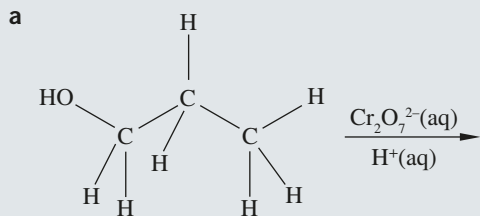


Chemical properties of alcohols

- 5 State the name of the functional group that will be formed in reactions of the following types of alcohols with potassium permanganate solution. If there is more than one possible product, state both names.
- a Primary alcohol
b Secondary alcohol
c Tertiary alcohol
- 6 Write the structural formulas of all the possible products from the oxidation of the following alcohols.



- 7 Write the structural formulas of the organic reactants or products for the following reactions.



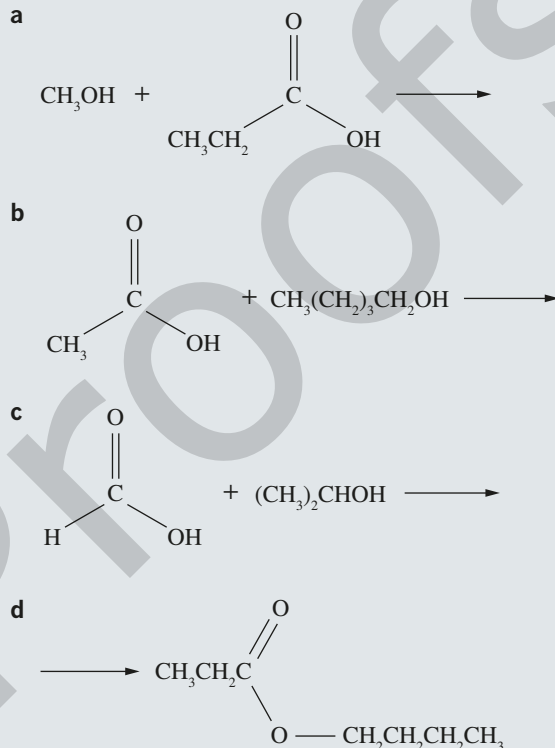
- c Pentan-2-ol heated with $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ solution
 d Butan-1-ol with $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ solution, mild heat; the product is distilled off as it forms.
- 8 Write a balanced redox equation for the reaction that occurs when propan-1-ol is heated with a solution of acidified potassium permanganate. Show the half-equations.
- 9 When using acidified potassium permanganate solution to determine if an unknown alcohol is primary, secondary or tertiary, the laboratory instructions state that the permanganate solution must be added dropwise to an excess of the alcohol. Explain why it is important that the permanganate solution is added dropwise to an excess of alcohol for this test to be successful.

Chemical properties of carboxylic acids

- 10 Write an ionic equation to show propanoic acid behaving as an acid in aqueous solution. Label the conjugate acid–base pairs. Comment on the relative concentrations you would expect for the reactants and products for this acid.
- 11 Give the names of the products when ethanoic acid is reacted with:
- zinc hydrogencarbonate
 - zinc oxide
 - zinc metal
 - zinc hydroxide.

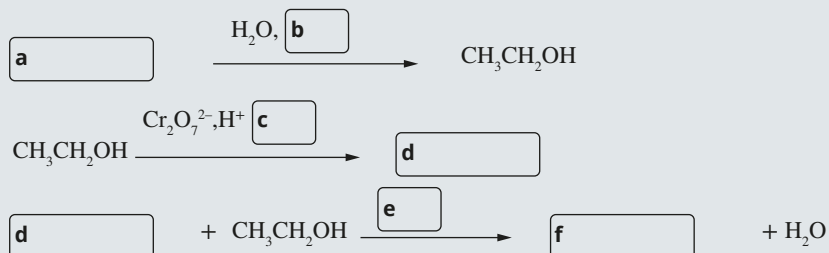
- 12 Write balanced equations for the reaction of:
- methanoic acid and solid sodium carbonate
 - $\text{CH}_3\text{CH}_2\text{COOH} + \text{Mg}(\text{OH})_2$

- 13 Complete the following reactions by writing semistructural formulas for the missing organic compounds.



Creating molecules: an introduction to organic synthesis

- 14 Complete the following reaction pathway for the formation of ethyl ethanoate by giving the formulas for the missing compounds.



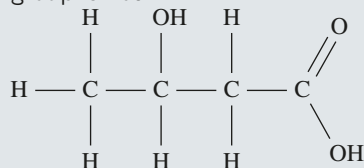
15 Consider the reaction pathway in which ethyl ethanoate is formed from ethene. List the reaction types in their correct order for this reaction pathway.

16 Ethyl propanoate can be manufactured from ethene as the only organic starting material. The ethene is converted to ethanol by hydration. Reaction of ethene with water and carbon monoxide gives propanoic acid as the only product. Write a balanced equation for the three steps in the conversion of ethene to ethyl propanoate.

Connecting the main ideas

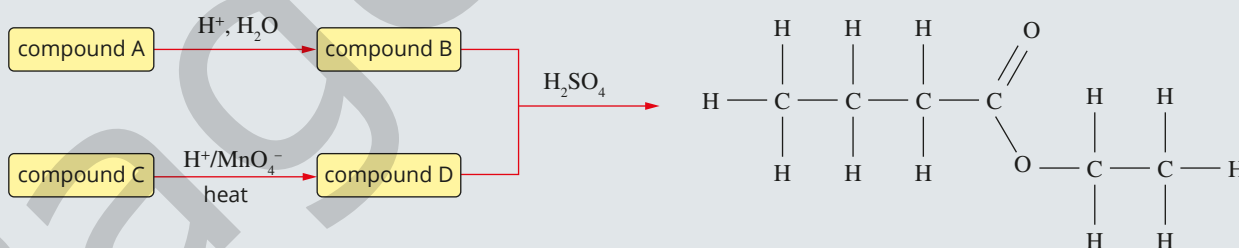
17 In the redox reactions of alcohols with permanganate and dichromate, the permanganate and dichromate solutions are acidified with sulfuric acid. In the condensation reaction of an alcohol with a carboxylic acid, sulfuric acid is also used. Explain the role of sulfuric acid in each of these reactions.

18 Organic compounds can contain more than one functional group. 3-Hydroxybutanoic acid (shown below) has a carboxylic acid functional group and a hydroxy (alcohol) functional group. When this compound is heated with acidified dichromate solution, the hydroxy group is oxidised but the carboxylic acid group is not.



a Write the structural formula and give the name of the functional group for the product of the oxidation.

b Explain why the carboxylic acid group is not oxidised.



19 The reaction for the production of ethanol from ethene is shown below.



$$\Delta H = -45 \text{ kJ mol}^{-1}$$

a Use equilibrium principles to suggest the conditions of temperature and pressure that will favour a high yield of ethanol. Explain your reasoning.

b The yield for the reaction is about 5% but can be increased by cooling the gases to condense the ethanol and removing it from the equilibrium mixture. The ethene gas is then recycled. This is continually repeated and in this way an overall yield of about 95% is achieved. Explain, with reference to appropriate chemistry principles, why cooling the equilibrium mixture will condense the ethanol but not the ethene.

20 The ester ethyl butanoate is used as a synthetic fruit flavouring and as a solvent in perfumes. The reaction pathway shown below leads to ethyl butanoate.

a Complete the pathway by writing the structural formulas for compounds A–D.

b Which compound would be expected to have greater water solubility: B or C? Explain your answer.

