samples of an alkane and an alkene are shaken together with bromine water at room temperature, you will see that the red-brown colour of the bromine water is immediately decolourized by the alkene but remains coloured in the alkane.

Alkenes also differ from alkanes in the colour of the flame when they burn. Because they have a higher ratio of carbon to hydrogen, alkenes contain much more unburned carbon than alkanes when they burn in similar conditions. This gives them a much dirtier, smokier flame. By comparison aromatic compounds – those containing the benzene ring – are highly unsaturated and so burn with an even smokier flame.

Alkene test. Demonstration of the result of testing an alkane (hexane) and an alkene (hex-1-ene) with bromine water. The brown colour of the bromine water has been decolourized by the alkene, because it reacted with the carbon–carbon double bond in an addition reaction. No colour change occurs with the alkane, as it is a saturated molecule and is unable to undergo an addition reaction with bromine.

Polymerization of alkenes

Because alkenes readily undergo addition reactions by breaking their double bonds, they can be joined together to produce long chains known as **polymers**. The alkene used in this reaction is known as the **monomer** and its chemical nature will determine the properties of the polymer. Polymers, typically containing thousands of molecules of the monomer, are a major product of the organic chemical industry. Indeed many of our most common and useful plastics are polymers of alkenes.

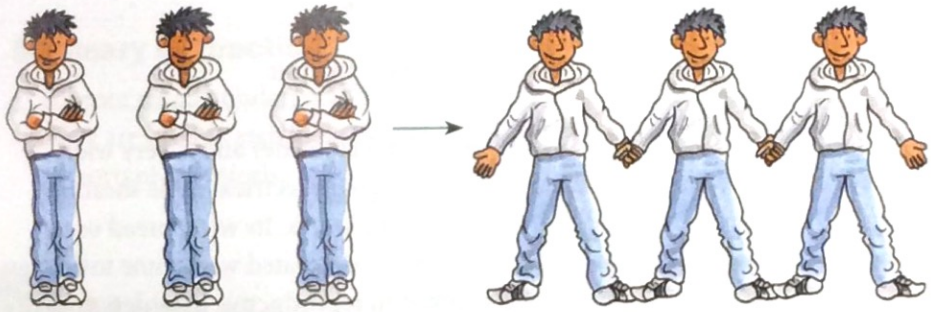
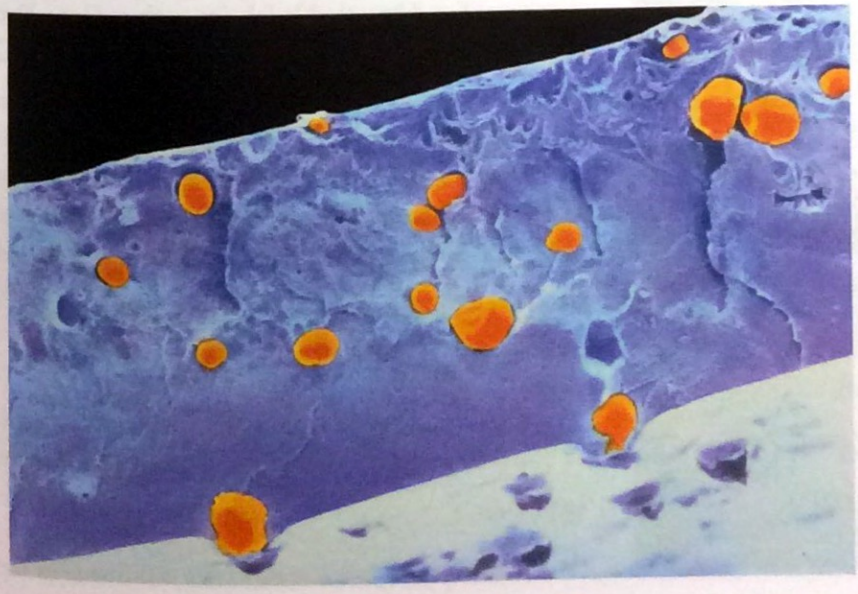
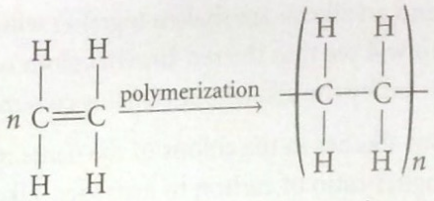


Figure 10.2 People cannot form a chain until they unfold their arms to release their hands. In the same way, alkenes must break their double bonds in order to join with other molecules in the polymer.

For example, ethene polymerizes to form poly-ethene, commonly known as polythene. This molecule was first synthesized in 1935, in a process which was discovered largely by accidental contamination of the reactants with oxygen. It has excellent electrical insulating properties and played an essential role in the development of radar during the Second World War. It is commonly used in household containers, carrier bags, water tanks and piping.



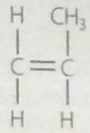
Coloured scanning electron micrograph of a section through a sheet of a biodegradable plastic. Many granules of starch (orange) can be clearly seen embedded in the plastic. When the plastic is buried in soil, the starch grains take up water and expand. This breaks the plastic into many small fragments, increasing the contact area with bacteria in the soil which digest the plastic. Such plastics help to address the major problem of waste plastic disposal.



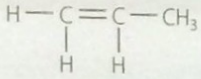
Similarly propene polymerizes to form polypropene, often called polypropylene. This polymer is used in the manufacture of clothing, especially thermal wear for outdoor activities.

● **Examiner's hint:** Note that when you are drawing these polymerization reactions, it is easiest to put the double bond in the *middle* of the structure, with the other groups above and below

like this



not like this

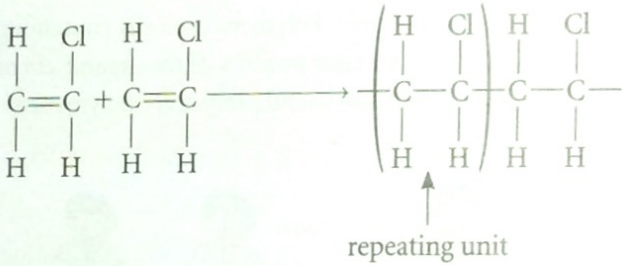


Then you can see how they can link together when the double bond breaks. Draw the two monomers side by side with exactly the same representation (as if you had used the 'copy' and 'paste' functions of a computer). Then just bond them together and see the repeating pattern.

Worked example

Show the reaction of polymerization of the monomer chloroethene, identifying the repeating unit.

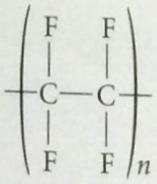
Solution

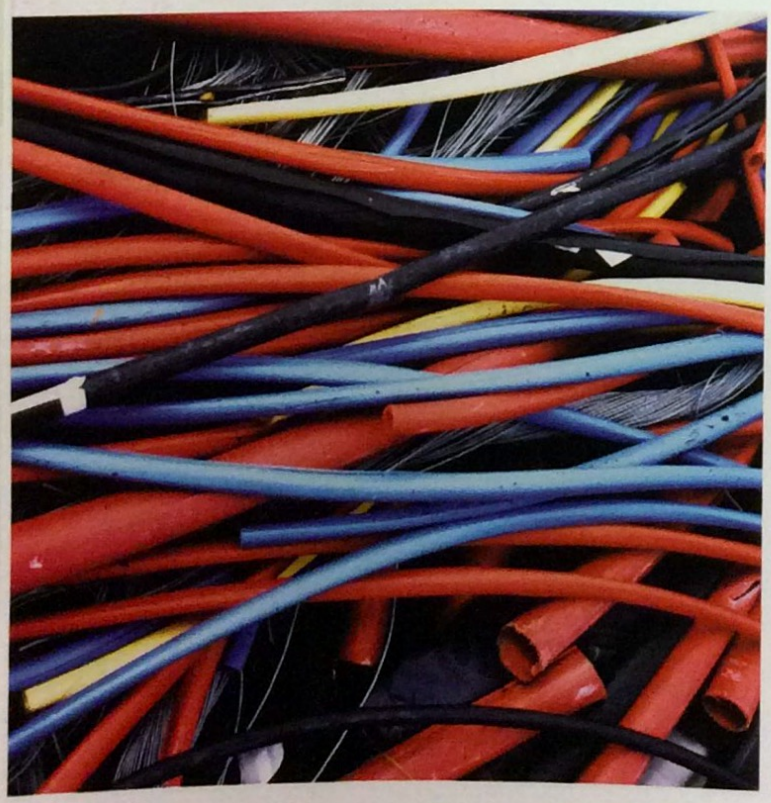


Take part in 'The great PVC controversy'.
Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

Polychloroethene is also known as PVC (poly vinyl chloride) and is very widely used in all forms of construction materials, packaging, electrical cable sheathing and so on. It is one of the world's most important plastics. Its widespread use is, however, somewhat controversial as its synthesis is associated with some toxic by-products known as dioxins, which are linked to reproductive disorders and a variety of cancers. The environmentalist group Greenpeace has advocated the global phase out of PVC.

Another interesting polymer is known as PTFE – polytetrafluoroethene. Because of its non-adhesive surface properties, it is widely used in non-stick pans under registered trademark names such as Teflon®. It also comprises one of the layers in the manufacture of waterproof and breathable fabrics such as Gore-Tex®. Its structure is:





Waste dumping of PVC – a major environmental problem.

Coloured scanning electron micrograph of Gore-Tex® fabric used to make water-proof clothing. The pink layers on top and bottom are nylon, while the filling shown in yellow/white is made from Teflon. This forms a microporous membrane containing pores less than a micrometre in diameter, 20 000 times smaller than a *drop* of water but 700 times larger than a water *molecule*. So the fabric allows water vapour to move outwards from the body, without allowing the penetration of liquid water inwards. Clothing made from this fabric is thus known as 'breathable waterproofing'.

Summary of reactions of alkenes

- Alkenes readily undergo addition reactions.
- They are used as starting materials in the manufacture of many industrially important chemicals.

10.4 Alcohols

- General formula $C_nH_{2n+1}OH$
- Alcohols have the –OH functional group. As this is a polar group, it increases the solubility in water of the molecules relative to the corresponding alkanes. The most common alcohol, ethanol C_2H_5OH, is readily soluble in water, as we know from its presence in alcoholic drinks.

Combustion

Like the hydrocarbons, alcohols burn in oxygen to form carbon dioxide and water with the release of significant amounts of energy. Indeed, alcohols are an important source of fuel and are used in alcohol burners and similar heaters. The amount of energy released per mole of alcohol increases as we go up the homologous series, chiefly due to the increasing number of carbon dioxide molecules produced.

For example, the burning of methanol can be represented as follows:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

which means it has a 1:1 ratio of CO_2:alcohol and $\Delta H^{\theta}_c = 726.1$ kJ mol^{-1}, whereas the burning of pentanol can be represented as follows:

$$2C_5H_{11}OH(g) + 15O_2(g) \rightarrow 10CO_2(g) + 12H_2O(g)$$

which means it has a 5:1 ratio of CO_2:alcohol and $\Delta H^{\theta}_c = 3330.9$ kJ mol^{-1}.

Alcohol burner: the flame is burning on a wick that is soaked in ethanol. Alcohols burn with a relatively clean (non-sooty) flame so are useful as fuels.

Methanol is considered to be a potential candidate to replace fuels based on crude oil. It can be burned directly as a fuel, or used in the production of hydrogen for fuel cells. It is synthesized on a large scale by the reduction of carbon dioxide and carbon monoxide.

As is the case with the hydrocarbons, in the presence of a limited supply of oxygen alcohols will produce carbon monoxide instead of carbon dioxide.

In New York City, a methanol-powered bus drives down the street. Methanol, CH_3OH, is a clear and colourless liquid used as a hydrogen carrier for fuel cells. Methanol fuel cells will reduce the dependence on petroleum and improve urban air quality.

Oxidation

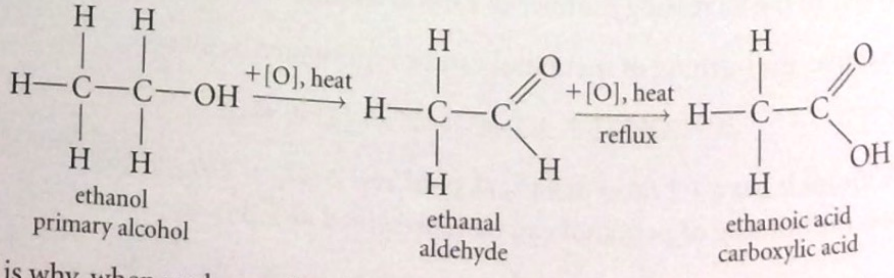
Although combustion involves the *complete* oxidation of the alcohol molecules, it is also possible for them to react with oxidizing agents which selectively oxidize the carbon atom attached to the –OH group, keeping the carbon skeleton of the molecule intact. In this way, alcohols can be oxidized into other organic compounds of significance. The exact nature of these reactions is determined by the class of alcohol, as we described in Section 10. 1.

Various oxidizing agents can be used for these reactions, but the one most commonly used in the laboratory is acidified potassium dichromate(VI) (see Chapter 9 for an explanation of oxidation numbers).This is a bright orange solution (owing to the presence of Cr(VI)). When the reaction mixture is heated, an obvious colour change is observed as the Cr(VI) is reduced to Cr(III) which is green, while the alcohol is oxidized. When writing these reactions it is often easier to show the oxidizing agent simply as +[O]. The oxidation reactions of the different alcohols are as follows.

Primary alcohols

Primary alcohols are oxidized in a two-step reaction, first forming the **aldehyde**, which is then oxidized further to the **carboxylic acid**.

For example:



This is why, when we leave a bottle of wine exposed to the air, bacteria slowly oxidize the ethanol to ethanoic acid, giving the smell of vinegar.

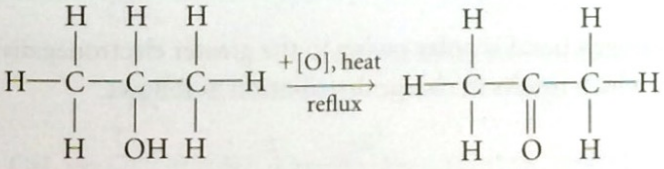
Distillation apparatus used to separate liquids with different boiling points. In the oxidation of a primary alcohol, it can be used to separate the first product, the aldehyde, from the reaction mixture and prevent its further oxidation to acid. The aldehyde has a lower boiling point than the carboxylic acid and so is collected as a gas and passes into the condensing tube. This is surrounded by cold flowing water, so the gas is condensed into a liquid which is collected in the beaker at the bottom.

Student heating a pear-shaped flask using a bunsen burner and a reflux condensor. This apparatus is used to oxidize a primary alcohol to completion – to the carboxylic acid. It is designed to collect and condense vapours that would escape from the reaction mixture, so enabling the volatile components to remain in the reaction for long enough to complete their reaction.

If we want to obtain the aldehyde as the product, it is possible to remove it from the reaction mixture by distilling it off as it forms. This is possible because aldehydes have lower boiling points than either alcohols or carboxylic acids, owing to the fact that they do not have hydrogen bonding between their molecules. If, on the other hand, we want to obtain the carboxylic acid as the product, we must leave the aldehyde in contact with the oxidizing agent for a prolonged period of time. This will be achieved most efficiently if apparatus called a **reflux condensor** is used.

Secondary alcohols

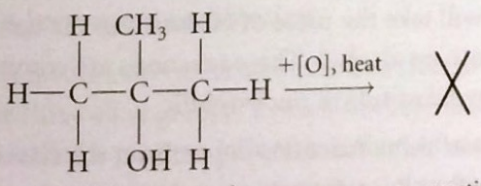
Secondary alcohols are oxidized to the **ketone** by a similar process of oxidation, for example:



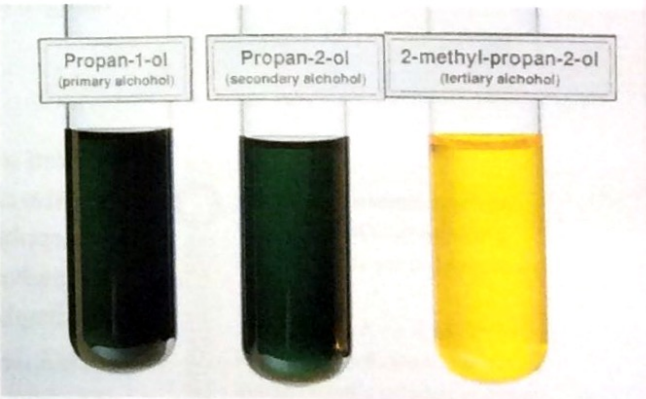
$CH_3CHOHCH_3$ propan-2-ol → $(CH_3)_2CO$ propanone

Tertiary alcohols

Tertiary alcohols are not readily oxidized under comparable conditions, as this would involve breaking the carbon skeleton of the molecule, which requires significantly more energy. Therefore we will not see a colour change in the potassium dichromate(VI) oxidizing agent when it is reacted with a tertiary alcohol, for example:



2-methylpropan-2-ol → no reaction



Oxidation of alcohols. Completed oxidation reactions of three alcohols with potassium dichromate solution ($K_2Cr_2O_7$, yellow). The dichromate is a strong oxidizing agent that is reduced when it reacts to form a green solution. Primary and secondary alcohols can be oxidized, forming carboxylic acids and ketones, respectively. Tertiary alcohols are not oxidized and do not react.