

# Chapter 18:

## Carbonyl compounds

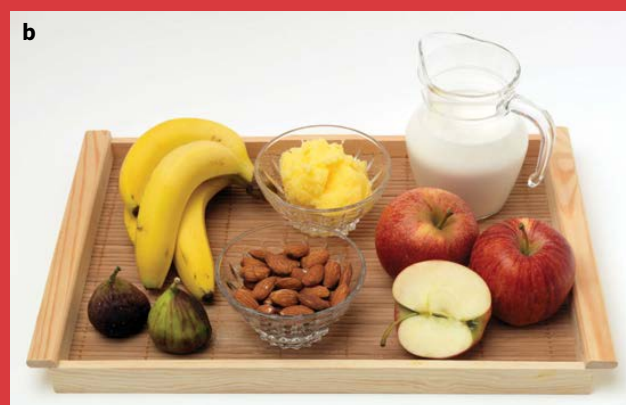
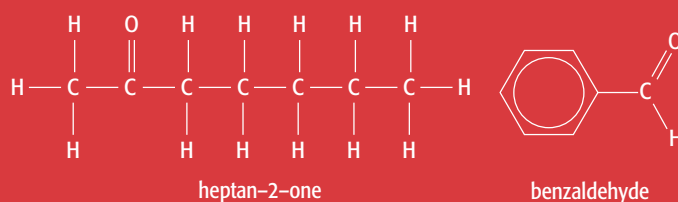
### Learning outcomes

You should be able to:

- describe:
  - the formation of aldehydes and ketones from oxidation of primary and secondary alcohols
  - the reduction of aldehydes and ketones, e.g. using  $\text{NaBH}_4$  or  $\text{LiAlH}_4$
  - the reaction of aldehydes and ketones with  $\text{HCN}$  and  $\text{NaCN}$
- describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide
- describe the detection of carbonyl compounds by the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent
- distinguish between aldehydes and ketones by testing with Fehling's and Tollens' reagents
- describe the reaction of  $\text{CH}_3\text{CO}-$  compounds with alkaline aqueous iodine to give tri-iodomethane
- deduce the presence of a  $\text{CH}_3\text{CH}(\text{OH})-$  group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane
- analyse an infra-red spectrum of a simple molecule to identify functional groups.

## Introduction

Aromatic carbonyl compounds have very distinctive, almond-like odours. Benzaldehyde is used to make almond essence, the flavouring used in some cakes and puddings. Benzaldehyde is also a component of the mixtures that make up the smells and flavours of many fruits such as mangoes, cherries, apricots, plums and peaches. The structures of heptan-2-one and benzaldehyde are shown on the right:



**Figure 18.1** **a** Heptan-2-one, a ketone, is responsible for the smell of blue cheese. **b** Benzaldehyde, an aldehyde, contributes to the flavours of many fruits and nuts. The structures of heptan-2-one and benzaldehyde are shown above by their displayed formulae.

## The homologous series of aldehydes and ketones

You have met aldehydes and ketones, the main classes of carbonyl compounds, in [Chapter 17](#). Remember:

- aldehydes can be formed from the oxidation of primary alcohols
- ketones can be formed from the oxidation of secondary alcohols (see page 236).

In aldehydes the carbon atom in the carbonyl group,  $C=O$ , is bonded to a carbon atom and a hydrogen atom. In other words, the carbonyl group is positioned at the end of a carbon chain.

In ketones the carbonyl group is attached to two other carbon atoms. [Tables 18.1](#) and [18.2](#) give examples from the start of these homologous series.

Name	Structural formula
methanal	$HCHO$
ethanal	$CH_3CHO$
propanal	$CH_3CH_2CHO$
butanal	$CH_3CH_2CH_2CHO$
pentanal	$CH_3CH_2CH_2CH_2CHO$

**Table 18.1** The names of aldehydes are derived from the name of the equivalent alkane, with the ‘-e’ at the end of the name replaced by ‘-al’. Note that numbers are not needed when naming aldehydes, as the carbonyl group is always at the end of the carbon chain.

Name	Structural formula
propanone	$CH_3COCH_3$
butanone	$CH_3COCH_2CH_3$
pentan-2-one	$CH_3COCH_2CH_2CH_3$
pentan-3-one	$CH_3CH_2COCH_2CH_3$

**Table 18.2** Ketones are named by replacing the ‘-e’ with ‘-one’. However, in ketone molecules larger than butanone we need to indicate the position of the carbonyl group.



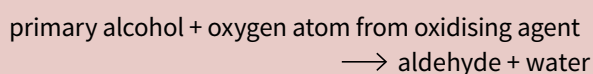
## QUESTION

- 1 a Name the following compounds:
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCH}_3$
- b Draw the displayed formula of:
- methanal
  - propanal
  - pentan-3-one.
- c Draw the skeletal formula of the compounds listed in part a.

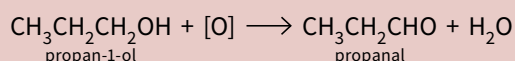
## Preparation of aldehydes and ketones

### 1 OXIDATION OF A PRIMARY ALCOHOL

The general equation for the reaction in which an aldehyde is made from a primary alcohol is:



For example:

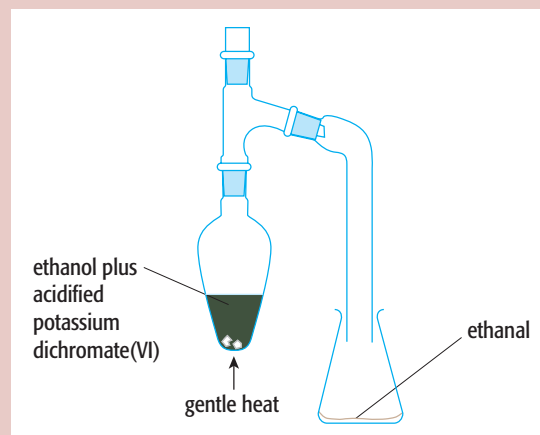


The oxidising agent used is a solution of potassium dichromate(VI), which is orange, acidified with dilute sulfuric acid. To make the aldehyde, the primary alcohol is heated gently with acidified dichromate solution. The reaction mixture turns green as the orange dichromate ions,  $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ , are reduced to green  $\text{Cr}^{3+}(\text{aq})$  ions.

The oxidising agent is added one drop at a time to the warm alcohol. The aldehyde made needs to be distilled off as it forms in the reaction vessel. This can be done because the aldehyde product will always have a lower boiling point than its corresponding alcohol. If the aldehyde is not distilled off as soon as it is formed, further heating

### 1 OXIDATION OF A PRIMARY ALCOHOL (CONTINUED)

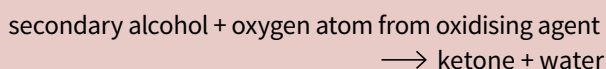
with acidified dichromate solution will oxidise the aldehyde produced to a carboxylic acid. The apparatus used to prepare a sample of ethanal is shown in Figure 18.2.



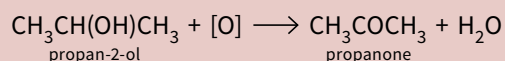
**Figure 18.2** Distilling off and collecting the aldehyde, ethanal, formed in the mild oxidation of a primary alcohol, ethanol. The aqueous ethanal formed smells like rotting apples.

### 2 OXIDATION OF A SECONDARY ALCOHOL

The general equation for making a ketone is:



For example:



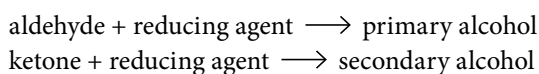
Once again, the oxidising agent used is a solution of potassium dichromate(VI), acidified with dilute sulfuric acid. To produce a ketone, this oxidising agent must be heated with a secondary alcohol. The ketone formed cannot be further oxidised, even if we reflux the reaction mixture and add excess oxidising agent. Therefore we do not need to distil out the ketone product immediately.

## QUESTION

- 2 a i** Write a balanced equation for the oxidation of ethanol to ethanal, using [O] to represent an oxygen atom from the oxidising agent.
- ii** Give practical details to explain how you would use the reaction described in part **a i** to prepare and collect a sample of ethanal.
- b i** Write a balanced equation for the oxidation of butan-2-ol to butanone, using [O] to represent an oxygen atom from the oxidising agent.
- ii** What do you observe in the reaction vessel if the oxidising agent used in part **b i** is potassium dichromate(VI) solution, acidified with dilute sulfuric acid, and the reaction mixture is heated?

## Reduction of aldehydes and ketones

Chemical reduction of an aldehyde or ketone produces an alcohol.

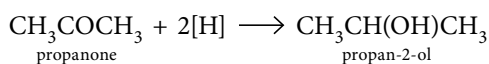
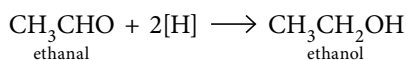


The reducing agent used is usually an aqueous alkaline solution of sodium tetrahydridoborate,  $\text{NaBH}_4$ , or lithium tetrahydridoaluminate,  $\text{LiAlH}_4$ , in dry ether.

The reduction reaction is carried out by either:

- warming the aldehyde or ketone with an aqueous alkaline solution of sodium tetrahydridoborate
- adding lithium tetrahydridoaluminate dissolved in a dry ether, such as diethyl ether, at room temperature. The organic solvent has to be dry because lithium tetrahydridoaluminate is a more powerful reducing agent than sodium tetrahydridoborate and reacts vigorously in water.

In the same way that we have used the symbol [O] in organic oxidation equations, we use the symbol [H] in reduction equations. [H] represents a hydrogen atom from the reducing agent. Look at the equations below used to summarise these reduction reactions:

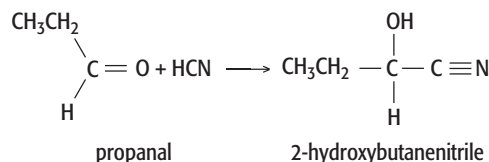


## QUESTION

- 3 a** Write a balanced equation for the reaction that takes place when propanal is warmed with an aqueous alkaline solution of sodium tetrahydridoborate, using the symbol [H] to represent a hydrogen atom from the reducing agent.
- b** Name the product formed in the reduction reaction if pentan-3-one is added to lithium tetrahydridoaluminate in dry ether.

## Nucleophilic addition with HCN

The addition reactions we have met so far have involved electrophilic addition across the  $\text{C}=\text{C}$  bond in alkene molecules (see page 209). Aldehydes and ketones both undergo addition reactions with hydrogen cyanide, HCN. In this case, addition of HCN takes place across the  $\text{C}=\text{O}$  bond. However, the attack is by a nucleophile, not an electrophile. We can show this using the **nucleophilic addition** reaction of propanal with HCN. The HCN is generated *in situ* (in the reaction vessel) by the reaction of sodium cyanide, NaCN, and dilute sulfuric acid.

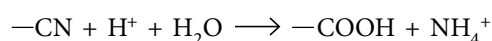


Note that a carbon atom has been added to the propanal molecule by the addition of the nitrile group ( $-\text{C}\equiv\text{N}$ ). This is a useful reaction in synthetic chemistry, as it increases the length of the hydrocarbon chain in the original aldehyde molecule by one carbon atom.

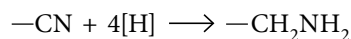
The nitrile group ( $-\text{C}\equiv\text{N}$ ) can then be easily:

- hydrolysed to a carboxylic acid
- reduced to an amine.

The hydrolysis can be carried out by refluxing with dilute hydrochloric acid:



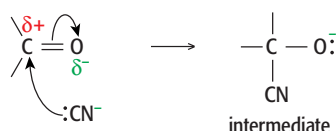
The reduction of the nitrile group to an amine can be carried out using sodium and ethanol:



## Mechanism of nucleophilic addition

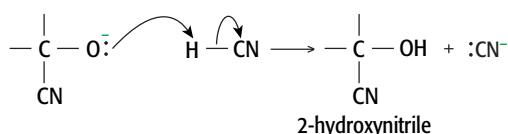
The carbonyl group,  $C=O$ , in aldehydes and ketones is polarised due to the high electronegativity of the oxygen atom. The electrons in the  $C=O$  bond are drawn nearer to the O atom, giving it a partial negative charge and leaving the C atom with a partial positive charge. This makes the C atom open to attack by a nucleophile, such as the cyanide ion,  $CN^-$ .

### First step



The negatively charged intermediate formed in the first step in the mechanism is highly reactive and quickly reacts with an  $H^+$  ion (from HCN, from dilute acid or from water present in the reaction mixture). This forms the **2-hydroxynitrile** product.

### Second step



All aldehydes and ketones form '2-hydroxynitriles' when they undergo nucleophilic addition as the  $-OH$  (hydroxyl) group will always be on the adjacent carbon atom to the nitrile group.

However, starting with the aldehyde methanal,  $HCHO$ , the hydroxynitrile formed in its nucleophilic addition with HCN would be called hydroxyethanenitrile. In this case there is no need to insert the '2' at the start of its name as the  $-OH$  group could only possibly bond to the carbon atom that is next to the nitrile group.

### QUESTION

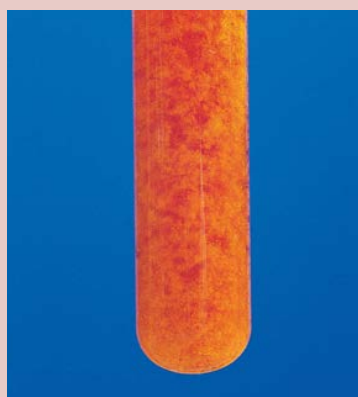
- 4 a Name the organic product that would be formed in the nucleophilic addition of HCN to:
- ethanal
  - propanone.
- b Use diagrams and curly arrows to describe the mechanism of the reaction in part a i.

## Testing for aldehydes and ketones

### Testing for the carbonyl group

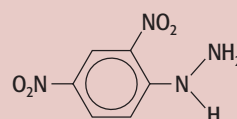
#### TESTING WITH 2,4-DNPH

The presence of a carbonyl group in an aldehyde or ketone can be easily tested for by adding a solution of 2,4-dinitrophenylhydrazine (often abbreviated to 2,4-DNPH). If an aldehyde or ketone is present, a deep-orange precipitate is formed (Figure 18.3).



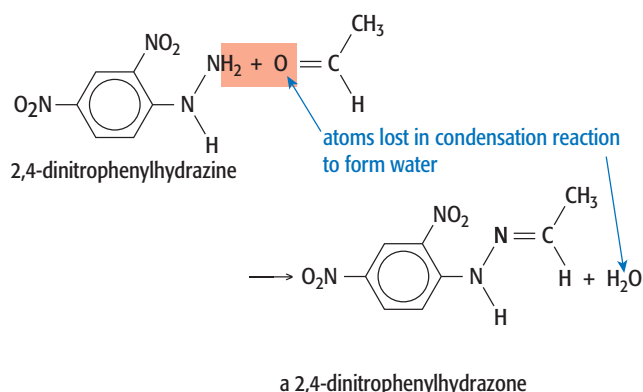
**Figure 18.3** The orange precipitate formed from 2,4-DNPH in a test with propanone, a ketone.

The structure of 2,4-dinitrophenylhydrazine is:



The precipitate formed can be purified by recrystallisation and its melting point can be measured experimentally. The identity of the compound that precipitated out can then be found by referring to melting point data. From this, the specific aldehyde or ketone used in the test can be identified.

The reaction of an aldehyde or ketone with 2,4-dinitrophenylhydrazine is an example of a **condensation reaction**. In a condensation reaction, two molecules join together and in the process eliminate a small molecule, in this case water. The equation for the reaction of ethanal with 2,4-DNPH is:



Other classes of organic compound that also contain the carbonyl group (such as carboxylic acids and esters) do not form precipitates.

## Distinguishing between aldehydes and ketones

As we saw on page 236, aldehydes can be further oxidised to form carboxylic acids, but ketones cannot be oxidised easily. We can use this difference to distinguish between an aldehyde and a ketone in simple chemical tests. The two tests most commonly used involve Tollens' reagent and Fehling's solution.

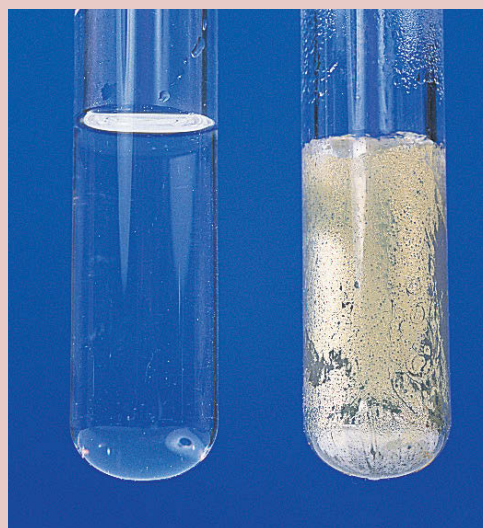
### TESTING WITH TOLLENS' REAGENT

**Tollens' reagent** is an aqueous solution of silver nitrate in excess ammonia solution, sometimes called ammoniacal silver nitrate solution. The silver ions,  $\text{Ag}^+$ , in the solution act as a mild oxidising agent. When warmed, the  $\text{Ag}^+$  ions will oxidise an aldehyde to form a carboxylate ion.

Under alkaline conditions any carboxylic acid formed is immediately neutralised to the carboxylate ion,  $\text{—COO}^-$ , as  $\text{H}^+$  is removed from  $\text{—COOH}$  and a salt is formed.

In the redox reaction with an aldehyde, the  $\text{Ag}^+$  ions themselves are reduced to silver atoms. The silver atoms form a 'mirror' on the inside of the tube, giving a positive test for an aldehyde (Figure 18.4).

There will be no change observed when a ketone is warmed with Tollens' reagent as no redox reaction takes place. It remains a colourless mixture in the test tube.



**Figure 18.4** The 'before' and 'after' observations when Tollens' reagent is warmed with an aldehyde, such as ethanal.

### TESTING WITH FEHLING'S SOLUTION

**Fehling's solution** is an alkaline solution containing copper(II) ions. When warmed with an aldehyde, the  $\text{Cu}^{2+}$  ions act as an oxidising agent. The aldehyde is oxidised to a carboxylate ion while the  $\text{Cu}^{2+}$  ions are reduced to  $\text{Cu}^+$  ions. The clear blue Fehling's solution turns an opaque red/orange colour as a precipitate of copper(I) oxide forms throughout the solution (Figure 18.5).

Once again, ketones are not oxidised, so the Fehling's solution remains blue when warmed.



**Figure 18.5** The 'before' and 'after' observations when Fehling's solution is warmed with an aldehyde, such as ethanal.

## QUESTION

- 5 The melting points of the derivatives of the reaction between 2,4-DNPH and various aldehydes and ketones are shown in the table.

Product of reaction between 2,4-DNPH and ...	Melting point / °C
ethanal	168
propanal	155
butanal	126
propanone	126
butanone	116

- a What would be observed when each of the carbonyl compounds in the table is mixed with 2,4-DNPH?
- b A derivative was formed between 2,4-DNPH and an unknown carbonyl compound.
- The melting point of the derivative was 126°C. What does this result tell you?
  - The unknown carbonyl compound formed an orange precipitate when warmed with Fehling's solution. Name the unknown compound.
  - Describe and explain the different results obtained when the compound named in part b ii is warmed with Tollens' reagent in a test tube and then the same test is performed on butanone.
- c Write a half-equation to show silver ions acting as an oxidising agent in a positive test for an aldehyde.
- d Write a half-equation to show copper(II) ions acting as an oxidising agent in a positive test for an aldehyde.



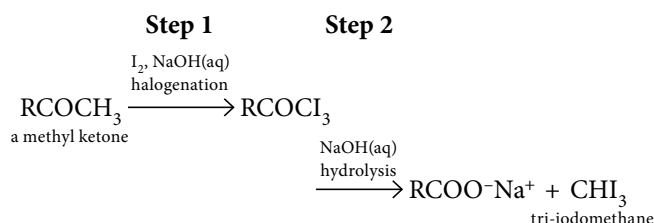
Figure 18.6 The yellow precipitate of tri-iodomethane forming.

The reaction involves two steps:

- the carbonyl compound is halogenated – the three hydrogen atoms in the  $\text{CH}_3$  group are replaced by iodine atoms
- the intermediate is hydrolysed to form the yellow precipitate of tri-iodomethane,  $\text{CHI}_3$  (Figure 18.6).

When separated from the reaction mixture, the yellow crystals of tri-iodomethane can be positively identified by their melting point of 119°C.

Here R is an alkyl group in a methyl ketone:



## Reactions to form tri-iodomethane

Tri-iodomethane (iodoform) forms as a yellow precipitate with methyl ketones, i.e. compounds containing the  $\text{CH}_3\text{CO}-$  group (Figure 18.6). Note that ethanal,  $\text{CH}_3\text{CHO}$ , an aldehyde, also contains the  $\text{CH}_3\text{CO}-$  group. Chemists use the appearance of the yellow precipitate as evidence of the  $\text{CH}_3\text{CO}-$  group in an unknown compound.

The reagent used is an alkaline solution of iodine, which is warmed together with the substance being tested.

## Testing for the $\text{CH}_3\text{CH}(\text{OH})-$ group

The tri-iodomethane test can also be used to identify the presence of a secondary alcohol group on the carbon atom adjacent to a methyl group. This  $\text{CH}_3\text{CH}(\text{OH})-$  group is firstly oxidised by the alkaline iodine solution. This oxidation forms a methyl ketone,  $\text{RCOCH}_3$ , which then reacts via the two steps shown above to give the yellow tri-iodomethane precipitate,  $\text{CHI}_3$ .

You should note that there are two organic products formed in this reaction: one is tri-iodomethane and the other is the sodium salt of a carboxylic acid.



## QUESTION

- 6 a i When propanone is warmed with alkaline iodine solution, a yellow precipitate is formed. Name and draw the displayed formula of the yellow precipitate.
- ii Give the structural formulae of the organic products formed in both steps of the reaction in part i.
- b Explain, naming any organic products formed, why ethanol gives a positive test when warmed with alkaline iodine solution.
- c Which of these compounds will give a yellow precipitate when treated with alkaline aqueous iodine?
- |                  |                 |
|------------------|-----------------|
| i butanone       | iv pentan-2-one |
| ii butanal       | v ethanal       |
| iii pentan-3-one | vi methanal     |

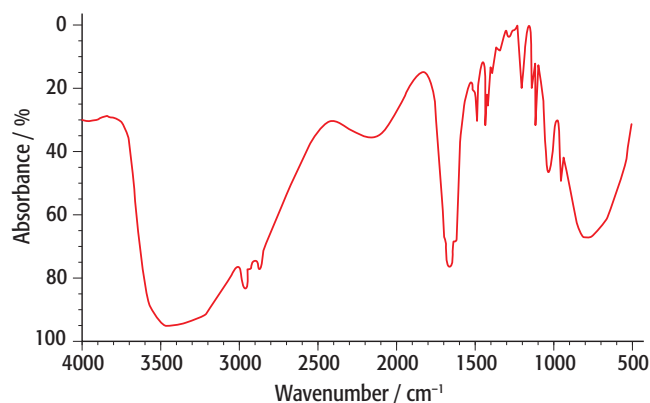
## Infra-red spectroscopy

In **infra-red spectroscopy** a sample being analysed is irradiated with electromagnetic waves in the infra-red region of the electromagnetic spectrum. The machine used is called a spectrophotometer, and it detects the intensity of the wavelengths of infra-red radiation that passes through the sample.

This analytical technique is particularly useful for organic chemists because all organic molecules absorb radiation in the infra-red range of wavelengths. The energy absorbed corresponds to changes in the vibration of the bonds between atoms. The bonds can vibrate by stretching, bending and twisting. They have a natural frequency at which they vibrate. If we irradiate the molecules with energy that corresponds to this frequency, it stimulates larger vibrations and energy is absorbed. This is called the **resonance frequency** of that vibration.

Each type of vibration will absorb characteristic wavelengths of infra-red radiation. These are often expressed as the reciprocal of the wavelength in a unit called wavenumbers (measured in  $\text{cm}^{-1}$ ). We cannot be too specific when quoting the characteristic absorption frequency of a bond – the nature of the rest of the molecule shifts the energy absorbed in each particular molecule. However, we can say, for example, that the amine group ( $-\text{NH}_2$ ) absorbs in the range 3300 to 3500  $\text{cm}^{-1}$ .

Therefore we can identify the presence (or absence) of different functional groups from the absorbance pattern on an infra-red spectrum. Look at the infra-red spectrum of ethylamine in Figure 18.7:



**Figure 18.7** The infra-red spectrum of ethylamine,  $\text{CH}_3\text{CH}_2\text{NH}_2$ . Note that the percentage absorbance and the wavenumbers on the axes both get smaller in magnitude along each axis.

We can use the characteristic infra-red spectrum of an unknown compound to identify it by ‘fingerprinting’ from a database of known spectra. Some characteristic absorption ranges and appearances of the peaks are shown in Table 18.3.

Bond	Functional groups containing the bond	Absorption range (in wavenumbers) / $\text{cm}^{-1}$	Appearance of peak ( <i>s</i> = strong, <i>w</i> = weak)
C—O	alcohols, ethers, esters	1040–1300	<i>s</i>
C=C	aromatic compounds, alkenes	1500–1680	<i>w</i> unless conjugated
C=O	amides ketones and aldehydes esters	1640–1690 1670–1740 1715–1750	<i>s</i> <i>s</i> <i>s</i>
C≡C	alkynes	2150–2250	<i>w</i> unless conjugated
C≡N	nitriles	2200–2250	<i>w</i>
C—H	alkanes, $\text{CH}_2-\text{H}$ alkenes/arenes, $=\text{C}-\text{H}$	2850–2950 3000–3100	<i>s</i> <i>w</i>
N—H	amines, amides	3300–3500	<i>w</i>
O—H	carboxylic acids, $\text{RCO}_2-\text{H}$ H-bonded alcohol, $\text{RO}-\text{H}$ free alcohol, $\text{RO}-\text{H}$	2500–3000 3200–3600 3580–3650	<i>s</i> and very broad <i>s</i> <i>s</i> and sharp

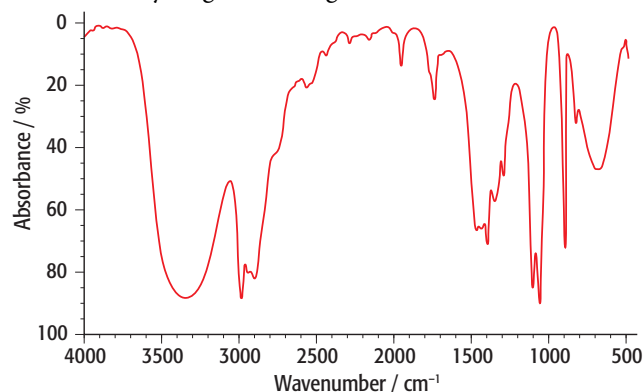
**Table 18.3** Some characteristic infra-red absorbance bands and their intensities.



These values will usually be given to you. You can see that absorption bands overlap considerably. That is why we need to use a variety of techniques, such as NMR, infra-red spectroscopy and mass spectrometry, to work out the structure of a new organic compound (see Chapter 29).

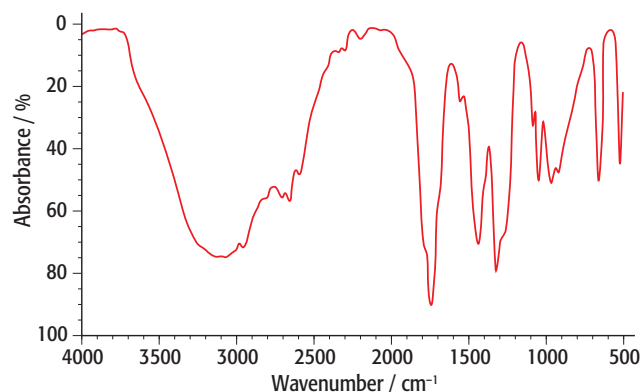
As well as their wavenumber bands, particular absorbances have characteristic widths (broad or sharp peaks) and intensities (strong or weak) on the infra-red spectrum. For example, the presence of hydrogen bonding makes the absorbance of the O—H bonds in alcohols and carboxylic acids broad. By contrast, the C=O bond in carbonyl groups has a strong, sharp absorbance peak. Look at the infra-red spectra of ethanol, ethanoic acid and ethyl ethanoate shown in Figures 18.8–18.10.

Using the data in Table 18.3, note the broad bands in Figures 18.8 and 18.9 arising from the O—H groups involved in hydrogen bonding in the alcohol and in the

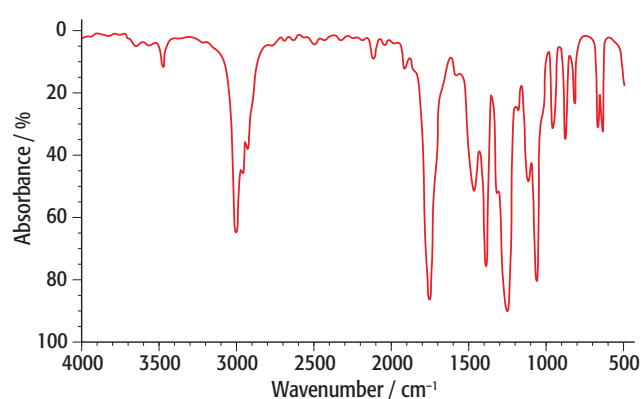


**Figure 18.8** The infra-red spectrum of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ .

carboxylic acid. Contrast the width of these peaks with the sharp peak of the carbonyl group in the ester, ethyl ethanoate in Figure 18.10.



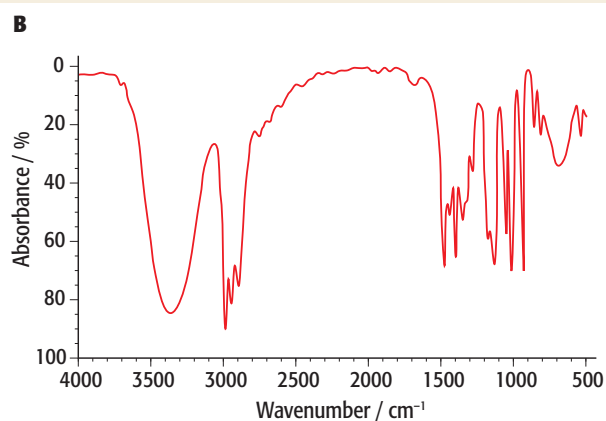
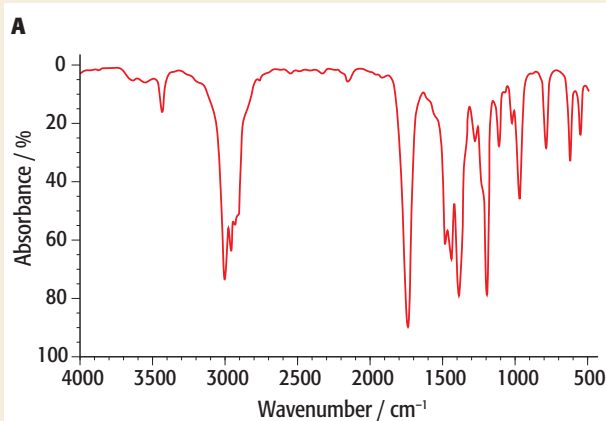
**Figure 18.9** The infra-red spectrum of ethanoic acid,  $\text{CH}_3\text{COOH}$ .



**Figure 18.10** The infra-red spectrum of ethyl ethanoate,  $\text{CH}_3\text{COOCH}_2\text{CH}_3$ .

## QUESTION

7 Look at the two infra-red spectra below:



- Which one of the infra-red spectra is that of butanone and which one is of butan-2-ol?
- Explain your reasoning in part a.

## Summary

- Aldehydes and ketones contain the carbonyl group,  $C=O$ :
  - in aldehydes, the carbonyl group is joined to just one other carbon atom
  - in ketones, the carbonyl group is joined to two other carbon atoms.
- The names of aldehydes are derived from the name of the alkane with the ‘-e’ at the end replaced by ‘-al’.
- Similarly, ketones are named with the ‘-e’ replaced by ‘-one’.
- Carbonyl compounds are readily reduced by aqueous  $NaBH_4$  or  $LiAlH_4$  dissolved in dry ether:
  - reduction of an aldehyde forms a primary alcohol
  - reduction of a ketone produces a secondary alcohol.
- Aldehydes are readily oxidised under mild conditions to carboxylic acids. Ketones are not oxidised under mild conditions.
- The polar nature of the carbonyl group in aldehydes and ketones enables them to undergo nucleophilic addition by reacting with the cyanide ions ( $CN^-$ ) from  $HCN$ . The product is a 2-hydroxynitrile.
- The reagent 2,4-dinitrophenylhydrazine (2,4-DNPH) can be used to identify the presence of a carbonyl group in an aldehyde or ketone. It produces an orange precipitate. The melting point of the product is used to identify particular aldehydes and ketones.
- As aldehydes are readily oxidised, they may be distinguished from ketones on warming with suitable oxidising reagents:
  - with aldehydes, Tollens’ reagent produces a silver mirror inside a warmed test tube and Fehling’s solution turns from a blue solution to a red/orange precipitate when warmed
  - with ketones, there is no oxidation reaction, so no changes are observed when ketones are warmed with Tollens’ reagent or Fehling’s solution.
- Chemists can use alkaline iodine solution to test for:
  - methyl ketones
  - ethanol or secondary alcohols with an adjacent methyl group.

A yellow precipitate of tri-iodomethane is formed in a positive test.
- Infra-red spectroscopy helps to identify organic compounds by their absorption of energy in the infra-red range of wavelengths, matching their spectrum to a database of known infra-red spectra.

## End-of-chapter questions

- 1 a Name the following compounds:
- |                     |     |
|---------------------|-----|
| i $CH_3COCH_3$      | [1] |
| ii $CH_3CH_2CH_2OH$ | [1] |
| iii $CH_3CHO$       | [1] |
| iv $CH_3CH(OH)CH_3$ | [1] |
| v $CH_3COCH_2CH_3$  | [1] |
| vi $CH_3CH_2CHO$    | [1] |
- b Which of the compounds in part a are alcohols and which are carbonyl compounds? [1]
- c Which of the carbonyl compounds in part a are aldehydes and which are ketones? [1]

- d Two of the compounds in part a could be made by oxidising two of the others.
- i Identify these four compounds, stating which could be made from which. [4]
  - ii State the reagents and conditions you would use to carry out each oxidation and write a balanced chemical equation for each oxidation. [O] can be used in oxidation equations. [4]
- e Ethanol could be made by the reduction of one of the compounds in part a.
- i Identify which compound this is. [1]
  - ii State the reagent you would use to carry out the reduction. [1]
  - iii Write a balanced chemical equation for the reduction. [H] can be used in reduction equations. [1]

Total = 19

- 2 a What reagent would you add to an unknown compound to see if it contains a carbonyl group? [1]
- b What result would you get if the unknown compound did contain a carbonyl group? [1]
- c Why would it be useful to find the melting point of the product of this test? [1]

Total = 3

- 3 a Draw the skeletal formulae of:
- i pentan-2-one [1]
  - ii pentan-3-one [1]
  - iii pentanal. [1]
- b Describe the results you would expect to see if pentan-3-one and pentanal were separately treated with Tollens' reagent. Where a reaction takes place, name the organic product and name the type of reaction that takes place. [4]

Total = 7

- 4 Ethanol can be made from ethanal using sodium tetrahydridoborate(III) as a reducing agent.
- a Give the formula of sodium tetrahydridoborate(III). [1]
  - b What other reagent is necessary for the reaction to take place? [1]
  - c The reaction mechanism proceeds in a similar way to the steps in the reaction of ethanal with HCN, but the initial attack is by the  $\text{H}^-$  ion instead of the  $\text{CN}^-$  ion. The intermediate then gains an  $\text{H}^+$  ion from a water molecule to form the product, ethanol. Name the mechanism and describe it as fully as you can, using curly arrows to show the movement of electron pairs. [7]

Total = 9

- 5 A compound, X, has the following percentage composition: 66.7% carbon, 11.1% hydrogen and 22.2% oxygen.
- a Calculate the empirical formula of X. [3]
  - b The relative molecular mass of X is 72. Calculate the molecular formula. [1]
  - c Give the structural formulae and names of the three isomers of X that are carbonyl compounds. [3]
  - d Explain how you could identify X using chemical means. [5]

Total = 12