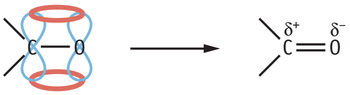
Carbonyl compounds Chapter 2

In AS Unit 2: Chains, energy and resources you encountered carbonyl compounds in the form of aldehydes and ketones and it is essential that you revisit some of the chemistry of alcohols. You will be expected to recall the preparation of carbonyl compounds from alcohols.

Aldehyde and ketone groups occur widely in sugars such as glucose and fructose, and they also contribute to the distinctive odours of many plants and foods.

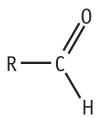
The carbonyl group is C=O and, like the C=C double bond, is formed by the overlap of adjacent *p*-orbitals. Like the alkenes, carbonyl compounds are unsaturated molecules. However, unlike alkenes, carbonyls are polar because of the difference in electronegativity between the carbon and oxygen atoms.



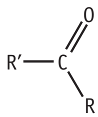
The *p*-orbitals overlap to form a π-bond

The position of the C=O on the carbon chain determines whether or not the compound is classified as an aldehyde or a ketone. An aldehyde has the carbonyl on the end of the carbon chain; in a ketone, the carbonyl group can be anywhere, other than on the terminal carbon atom.

An aldehyde contains the functional group:



Ketones look similar, but the functional group is:



(R and R′ = alkyl group, for example $–CH_3$ or $–CH_3CH_2$)

Formation of carbonyl compounds and carboxylic acids

These are formed by the oxidation of alcohols. The ease and extent of oxidation depends on the type of alcohol:

- Tertiary alcohols are resistant to oxidation.
- Primary and secondary alcohols undergo oxidation when warmed with an oxidising mixture such as acidified dichromate, $Cr_2O_7^{2-}/H^+$ (e.g. $K_2Cr_2O_7/H_2SO_4$).
  - A secondary alcohol is oxidised to a ketone.
  - A primary alcohol can be oxidised partially to an aldehyde or oxidised completely to a carboxylic acid.

The balanced equations for the oxidation of a primary alcohol to an aldehyde and of a secondary alcohol to a ketone are similar. Water is always formed and the equation can be represented as:

primary/secondary alcohol + [O] $\rightarrow$ carbonyl compound + water

Oxidation of a primary alcohol to an aldehyde

Methanol is oxidised to methanal:

$CH_3OH + [O] \rightarrow HCHO + H_2O$

Methanol Methanal

Ethanol is oxidised to ethanal:

$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$

Ethanol Ethanal

Oxidation of a secondary alcohol to a ketone

Propan-2-ol is oxidised to propanone (propan-2-one):

$CH_3CHOHCH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$

Propan-2-ol Propanone

Butan-2-ol is oxidised to butanone (butan-2-one):

$CH_3CH_2CHOHCH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O$

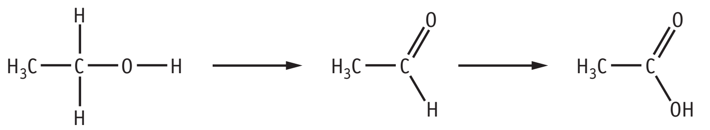
Butan-2-ol Butanone

Oxidation of a primary alcohol to a carboxylic acid

The primary alcohol is oxidised in two steps:

- The first step creates an aldehyde.
- In the second step, the second C–H bond is converted into a C–O–H.

Overall, the carboxylic acid functional group is generated:



Primary alcohol Aldehyde Carboxylic acid

All balanced equations for the oxidation of a primary alcohol to a carboxylic acid are similar. Water is always formed and the reaction can be represented as:

primary alcohol + 2[O] $\rightarrow$ carboxylic acid + water

Methanol is oxidised to methanoic acid:

$CH_3OH + 2[O] \rightarrow HCOOH + H_2O$

Methanol Methanoic acid

For exam purposes, the oxidising agent can be represented as [O] and the equation balanced as shown below. Full equations can be deduced using oxidation numbers and half-equations. This is covered in the additional reading and stretch-and-challenge questions at the end of this chapter.

Ethanol is oxidised to ethanoic acid:

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + 2[O] \rightarrow \underset{\text{Ethanoic acid}}{CH_3COOH} + H_2O$$

When oxidising a primary alcohol, such as propan-1-ol, the choice of apparatus is important. The alcohol and the oxidising mixture have to be heated. This can be achieved by either distillation (Figure 2.1) or reflux (Figure 2.2).

If propan-1-ol is oxidised it is possible to produce either propanal or propanoic acid. The boiling points are shown in Table 2.1.

***Table 2.1** Boiling points of propan-1-ol, propanal and propanoic acid*

Name	Formula	Boiling point/°C
Propan-1-ol	$CH_3CH_2CH_2OH$	97
Propanal	CH_3CH_2CHO	49
Propanoic acid	CH_3CH_2COOH	141

In general, alcohols and carboxylic acids have considerably higher boiling points than aldehydes. Alcohols and carboxylic acids both contain –O–H groups and therefore both form intermolecular hydrogen bonds.

e You will not be expected to recall any reactions of alcohols other than oxidation.

In order to isolate the aldehyde a distillation is usually carried out. Distillation involves evaporation followed by condensation and allows the most volatile component to be separated.

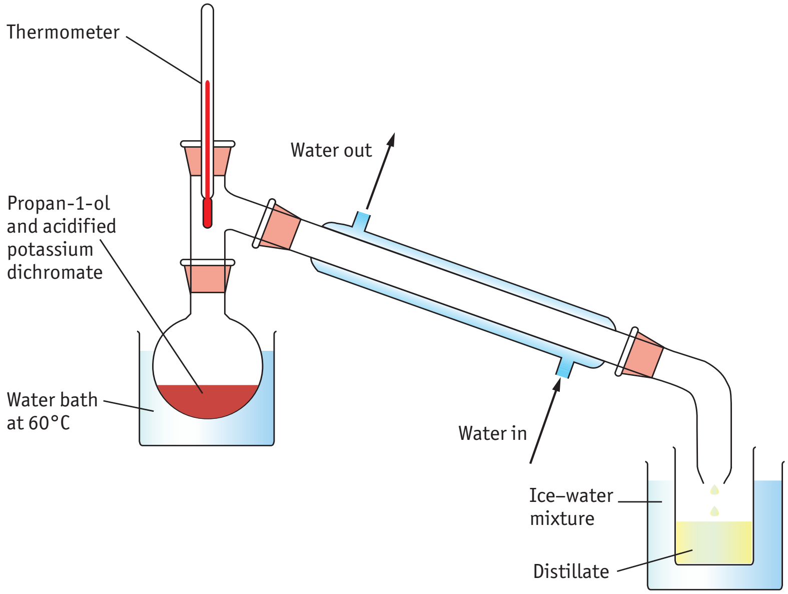


***Figure 2.1** Apparatus for distillation*

When the reaction mixture is heated, the volatile components evaporate first. Propanal has the lowest boiling point and vaporises most readily. The outer sleeve of the condenser contains circulating cold water, so when the propanal reaches the condenser, it condenses and is separated from the reaction mixture.

Reflux involves a process of continuous evaporation and condensation that prevents any volatile components from escaping.

If a reflux apparatus is used, the components undergo continuous evaporation and condensation and volatile components will not escape or be separated out. As with distillation, when the reaction mixture is heated the volatile components evaporate first. Propanal has the lowest boiling point and is vaporised most readily. The outer sleeve of the condenser contains circulating cold water, so when the propanal reaches the condenser, it condenses (as with distillation). However, it falls back into the oxidising mixture and is *not* separated from the reaction mixture. The propanal is then oxidised to form propanoic acid.

Any oxidation reaction that utilises the mixture of dichromate and sulphuric acid is accompanied by a distinctive colour change from orange to green. This occurs because orange dichromate ions, $Cr_2O_7^{2-}$, are reduced to green Cr^{3+} ions.

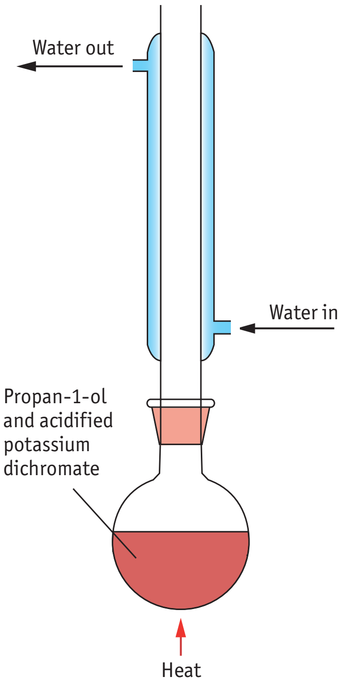


***Figure 2.2** Apparatus for reflux*

Reactions of carbonyl compounds

Aldehydes and ketones both contain the C=O group and therefore have some reactions in common. However, aldehydes can be oxidised easily whereas ketones cannot, so there are reactions that can be used to distinguish between them.

Reactions common to both aldehydes and ketones

Reduction

Aldehydes or ketones can be reduced to their respective alcohols using an aqueous solution of sodium tetrahydridoborate(III), $NaBH_4$, as the reducing agent.

[H] is used to represent the reducing agent in equations.

All balanced equations for the reduction of an aldehyde or a ketone are similar. The reaction can be represented as:

$$\text{aldehyde/ketone} + 2[H] \rightarrow \text{alcohol}$$

An aldehyde is reduced to a primary alcohol, for example:

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[H] \rightarrow \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH}$$

A ketone is reduced to a secondary alcohol:

$$\underset{\text{Propanone}}{CH_3COCH_3} + 2[H] \rightarrow \underset{\text{Propan-2-ol}}{CH_3CH(OH)CH_3}$$

The reduction can be regarded as a nucleophilic addition reaction with the reducing agent, $NaBH_4$, providing the hydride ion, $:H^-$, which behaves as a nucleophile.

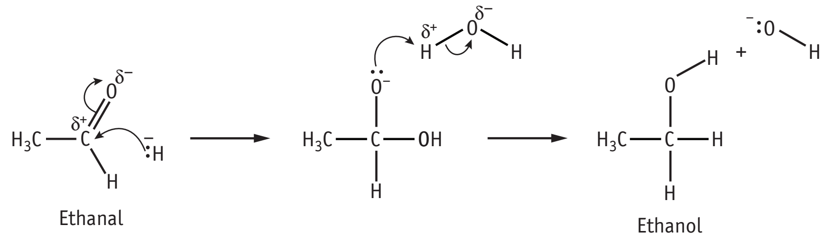
A nucleophile can be defined as an electron-pair donor.

Nucleophilic addition reactions

$^{\delta+}C{=}O^{\delta-}$ is a polar bond because the carbon and oxygen atoms have different electronegativities. The carbon in the carbonyl group is δ+ and can therefore be attacked by a nucleophile. The carbonyl group, C=O, is unsaturated and hence undergoes addition reactions. The mechanism is, therefore, nucleophilic addition.

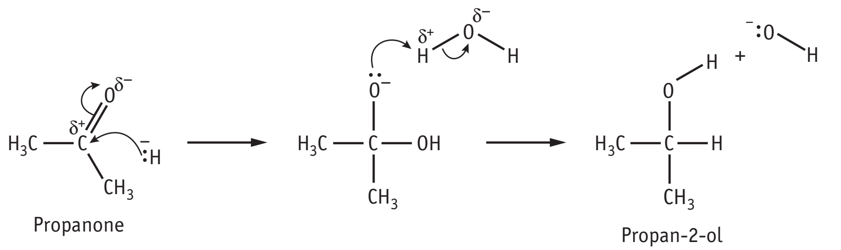
This is best illustrated by addition reactions with the hydride ion, H^-.

An example is the reduction of ethanal by aqueous $NaBH_4$:



When describing this mechanism you should show the movement of electrons by using curly arrows. You should also include relevant dipoles and lone pairs of electrons.

Ketones behave similarly — for example, the reduction of propanone by aqueous $NaBH_4$:



Reaction with 2,4-dinitrophenylhydrazine

Aldehydes and ketones both react with 2,4-dinitrophenylhydrazine.

Carbonyl compounds react with an excess of 2,4-dinitrophenylhydrazine to produce a bright red, orange or yellow precipitate. The precipitates formed are derivatives of 2,4-dinitrophenylhydrazine and are known as 2,4-dinitrophenylhydrazones.

The reactions of carbonyl compounds with 2,4-dinitrophenylhydrazine (2,4-DNPH) are important for several reasons:

NIGEL EVANS

A precipitate of 2,4-dinitrophenylhydrazine

You are not expected to recall the formula of 2,4-dinitrophenylhydrazine. The abbreviation 2,4-DNPH is acceptable.

The formula of 2,4-dinitrophenylhydrazine is used in the additional reading at the end of this chapter, where the reactions of aldehydes and ketones are explained in more detail

- 2,4-DNPH reacts with a carbonyl compound to produce a distinctive precipitate. The organic product is a bright red, orange or yellow precipitate. Therefore, this reaction can be used to identify the presence of a carbonyl group (aldehyde and ketone).
- The organic product (the 2,4-DNPH derivative) is relatively easy to purify by recrystallisation. The melting point of the brightly coloured precipitate can then be determined.
- Each derivative has a different melting point, which may be used to identify a specific carbonyl compound. Table 2.2 shows the melting points of the derivatives of a few common carbonyl compounds.

Table 2.2
Melting points of some carbonyl compounds

Carbonyl compound	Boiling point/°C	Melting point of the 2,4-DNPH derivative/°C
Ethanal	20	148
Propanal	49	156
Butanal	75	123
Methylpropanal	64	182
Propanone	56	128
Butanone	80	115
Pentan-2-one	102	142
Pentan-3-one	102	153
3-Methylbutan-2-one	94	124

The preparation and purification of a 2,4-dinitrophenylhydrazine derivative can be used to identify a specific aldehyde or ketone. The process involves the initial preparation of the derivative, which is filtered and then recrystallised and dried. The melting point of the derivative is then determined and checked against data values to identify the original carbonyl compound. This is particularly useful when trying to distinguish between isomers such as pentan-2-one and pentan-3-one, which have the same boiling point.

Reactions for aldehydes only

Aldehydes and ketones can be distinguished by a series of redox reactions. Aldehydes are oxidised readily to carboxylic acids; ketones are not oxidised easily.

There are three common oxidising mixtures that can be used.

(1) **Oxidising mixture**: acidified dichromate ($H^+/Cr_2O_7^{2-}$)

Conditions: warm

Observation: when reacted with an aldehyde there is a colour change from orange to green

(2) **Oxidising mixture**: alkaline solution of Cu^{2+} ions with an alkaline solution of potassium tartrate (Fehling's solution)

Conditions: warm gently in a water bath at about 60°C

Observation: Fehling's solution is a dark blue solution which when reacted with an aldehyde produces a red precipitate of copper(I) oxide, $Cu_2O(s)$

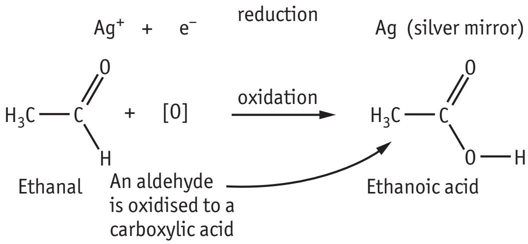
(3) **Oxidising mixture**: an aqueous solution of Ag^+ ions in excess ammonia, $Ag(NH_3)_2^+$ (Tollens' reagent)

Conditions: warm gently in a water bath at about 60°C

Observation: silver metal is precipitated forming a silver mirror

Tollens' reagent is prepared by adding a few drops of dilute sodium hydroxide solution to a solution of silver nitrate. A brown precipitate of silver oxide, $Ag_2O(s)$, is produced immediately. Dilute ammonia is then added until the $Ag_2O(s)$ just redissolves. This creates an ammoniacal solution of silver nitrate, $Ag(NH_3)_2^+$, which acts as the oxidising agent.

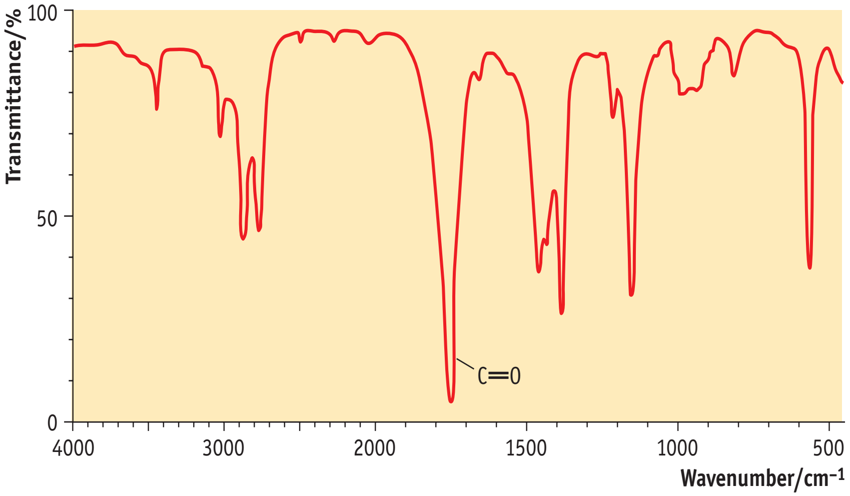
In this reaction, the Ag^+ ions are reduced to silver metal (electron gain) and the aldehyde is oxidised to a carboxylic acid. The reaction with ethanal is given below:



The oxidation of an aldehyde to a carboxylic acid can be identified using infrared spectroscopy.

The relevant absorptions to pick out are those of the C=O group which is present in both aldehydes and ketones and which has a strong absorption in the range 1640–1750 cm^{-1}. Carboxylic acids also have a C=O absorption but in addition have a characteristic broad absorption within the region 2500–3300 cm^{-1}, which is due to the O–H group in the carboxylic acid.

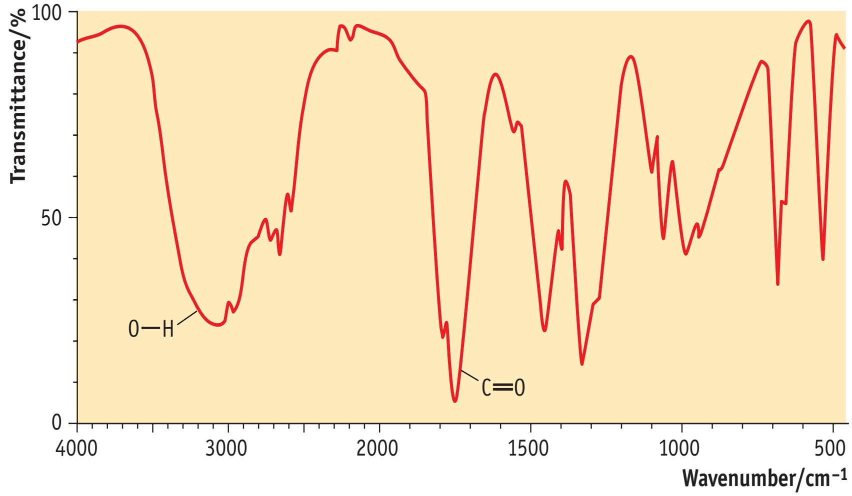
The absorption due to the carbonyl group can be seen clearly in the IR spectrum of ethanal:



The OCR specification recommends that you use Tollens' reagent to distinguish between an aldehyde and a ketone.

Infrared spectroscopy was first introduced in Unit 2: Chains, energy and resources (see the AS textbook, page 187).

The spectrum below shows the absorption for both the C=O and the O–H groups, confirming that the ethanal has been oxidised to ethanoic acid:



Questions

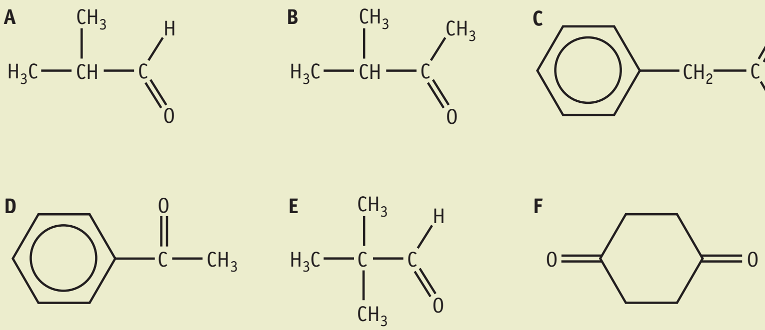
1 a Name each of the compounds **A**–**F**.

b Classify each of **A** to **F** as either an aldehyde or a ketone.

c What is the molecular formula of compound **F**?

d Identify the alcohols from which **C** and **D** could be prepared.

e Compounds **B** and **E** are isomers of each other. Draw the structures of three other isomers of **B** and **E**.



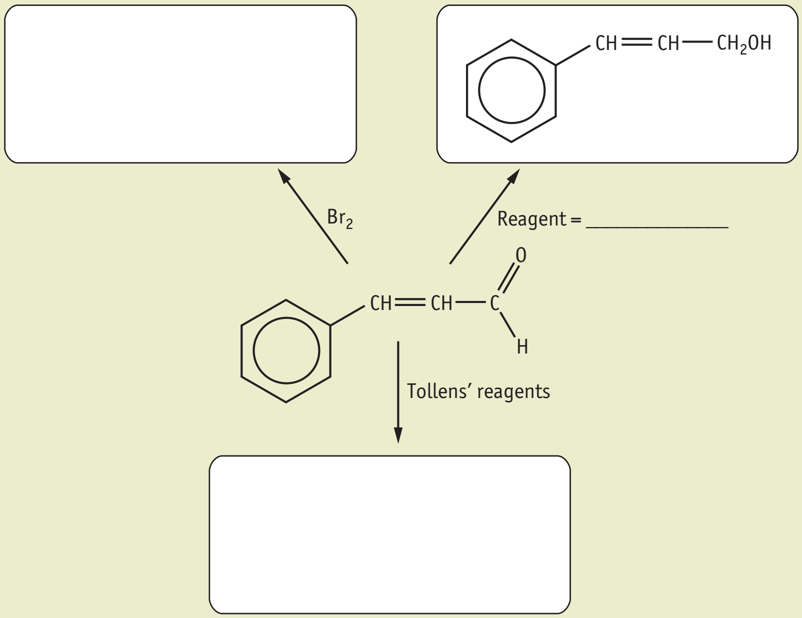
2 Butan-2-ol can be prepared by the reduction of a carbonyl compound. Identify the compound, state the reagents and conditions required, write a balanced equation and describe, with the aid of curly arrows, the mechanism.

3 Cinnamaldehyde, C_9H_8O, is a yellow liquid with a powerful odour.

a Complete the reaction grid below for the reactions of cinnamaldehyde.

b Write a balanced equation for the oxidation of cinnamaldehyde by Tollens' reagent.

c There are two possible isomers of cinnamaldehyde. Draw their structures and state the type of isomerism.



Summary

You should now be able to:

- distinguish between aldehydes and ketones
- write equations for the preparation of aldehydes and ketones by the oxidation of primary and secondary alcohols respectively
- describe the nucleophilic addition mechanism when aldehydes and ketones are reduced by $NaBH_4$(aq)
- describe the reactions of aldehydes and ketones with 2,4-dinitrophenylhydrazine and explain how the derivatives formed can be used to identify the carbonyl compounds
- describe how aldehydes react with Tollens' reagent

Additional reading

2

You are expected to recall the preparation of aldehydes and ketones by the oxidation of alcohols and to be able to write balanced equations using [O] to represent the oxidising agent. It is perfectly acceptable to simply learn these equations. However, with a little extension to your understanding of oxidation number, you should be able to work out the full equation from first principles using ionic half-equations.

You will recall that oxidation number can be assigned using a simple set of rules.

Rule number	Rule	Example
1	All elements in their natural state have the oxidation number zero	Hydrogen, H_2; oxidation number = 0
2	Oxidation numbers of the atoms of any molecule add up to zero	Water, H_2O; sum of oxidation numbers = 0
3	Oxidation numbers of the components of any ion add up to the charge on that ion	Sulphate, SO_4^{2-}, sum of oxidation numbers = −2

When calculating the oxidation numbers of elements in either a molecule or an ion you should apply the following order of priority:

1	The oxidation numbers of elements in groups 1, 2 and 3 are always +1, +2 and +3 respectively.
2	The oxidation number of fluorine is always −1.
3	The oxidation number of hydrogen is usually +1.
4	The oxidation number of oxygen is usually −2.
5	The oxidation number of chlorine is usually −1.

By applying these rules and priorities in sequence it is possible to deduce any oxidation number.

Consider the oxidation of ethanol to ethanal using acidified dichromate, $H^+/Cr_2O_7^{2-}$, in terms of oxidation number. Whenever we use an oxidising agent in the presence of an acid, water is formed. During the oxidation, there is a colour change from orange to green. The orange colour is due to the $Cr_2O_7^{2-}$ ion and the green colour is due to the Cr^{3+} ion. The oxidation number of Cr in $Cr_2O_7^{2-}$ is +6; the oxidation number of Cr in Cr^{3+} is +3. Using this, we can construct an ionic half-equation for the changes that take place for Cr.

When writing ionic half-equations, we must balance both symbols and charge.

It is sensible to first balance the charge. We know that the oxidation number of Cr changes from +6 to +3 and that for each Cr atom this involves gaining three electrons. Since there are two Cr atoms in $Cr_2O_7^{2-}$, a total of six electrons is required. We can now write:

$$Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+}$$

We now have to balance the symbols. You will recall that whenever an oxidising agent is used in the presence of an acid, water is formed. Since $Cr_2O_7^{2-}$ contains seven oxygens, $7H_2O$ are formed. This requires $14H^+$. Therefore, the ionic half-equation for the oxidation is:

$$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

For $Cr_2O_7^{2-}$, **rule 3** tells us that the oxidation numbers have to add up to −2 and **priority 4** tells us that O has priority over Cr.

Oxidation number = −2

↓

$Cr_2O_7^{2-}$

There are seven oxygen atoms giving a total of −14. Hence, the contribution of the two Cr atoms must add up +12. Therefore, the oxidation number of each Cr atom is +6.

We can use this concept of oxidation number and do the same for the oxidation of ethanol to ethanal. First, we have to work out the oxidation numbers. This is easier if we write the molecular formula:

Oxidation number = ? Oxidation number = +1 Oxidation number = −2

C_2H_5OH — molecular formula is C_2H_6O

e The oxidation numbers assigned to carbon are theoretical. It is worth remembering that carbon almost always forms four bonds.

There are six hydrogens, giving a total of +6 and one oxygen (−2). Hence, the contribution from the two carbon atoms must add up to −4, which means that the oxidation number of each carbon is −2.

For ethanal:

Oxidation number = ? Oxidation number = +1 Oxidation number = −2

CH_3CHO — molecular formula is C_2H_4O

There are four hydrogens, giving a total of +4 and one oxygen (−2). Hence, the contribution from the two carbon atoms must add up to −2, which means that the oxidation number of each carbon is −1.

Each carbon loses one electron:

$$C_2H_5OH \rightarrow CH_3CHO + 2e^-$$

In order to balance for symbol and charge we must add two H^+ to the right-hand side. So, the half-equation for the reduction is:

$$C_2H_5OH \rightarrow CH_3CHO + 2e^- + 2H^+$$

We can now combine the two ionic half-equations:

The half-equation for reduction is:

$$14H^+ + Cr_2O_7^{2-} + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

The half-equation for oxidation is:

$$C_2H_5OH \rightarrow CH_3CHO + 2e^- + 2H^+$$

It is essential that there is the same number of electrons in each equation. It follows that the second half-equation has to be multiplied by 3 to give:

$$3C_2H_5OH \rightarrow 3CH_3CHO + 6e^- + 6H^+$$

Adding the two equations gives:

$$14H^+ + Cr_2O_7^{2-} + 6e^- + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO + 6e^- + 6H^+$$

This can be simplified to:

$$8H^+ + Cr_2O_7^{2-} + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$$

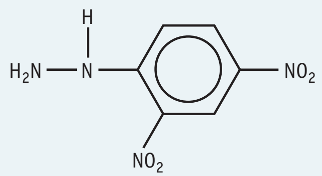
The $Cr_2O_7^{2-}$ came from $K_2Cr_2O_7$ and the H^+ came from H_2SO_4 so the full equation is:

$$4H_2SO_4 + K_2Cr_2O_7 + 3C_2H_5OH \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3CH_3CHO + K_2SO_4$$

e This is a difficult concept but it enables you to deduce complex equations. If you understand the process it will help greatly when you come to study electrode potentials in Unit 5.

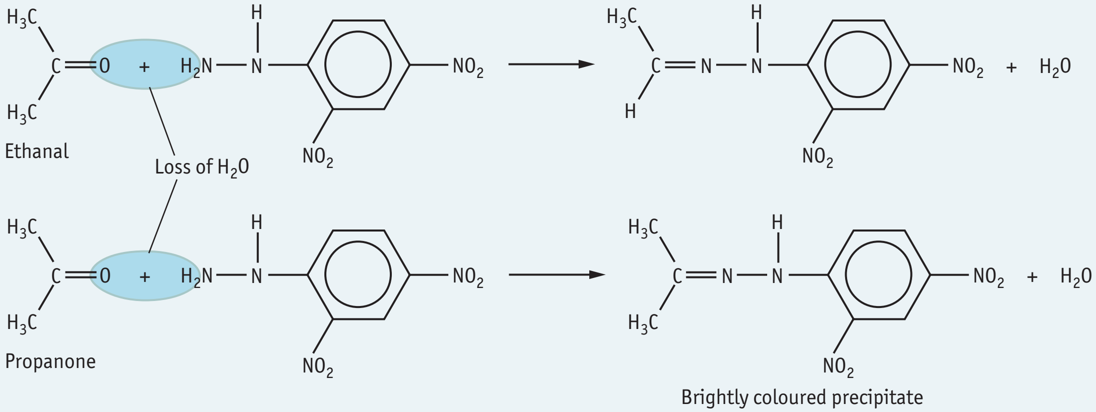
2,4-dinitrophenylhydrazine

The formula of 2,4-dinitrophenylhydrazine is:



It reacts with carbonyl compounds to produce brightly coloured precipitates.

The reaction between ethanal and propanone with 2,4-dinitrophenylhydrazine is shown below:



In this reaction, water is lost and it can be considered to be a condensation reaction.

e The specification does not require you to recall the formula or structure of 2,4-dinitrophenylhydrazine. However, knowledge of both may help with stretch-and-challenge questions.

Stretch and challenge

1 Write equations for the reaction between excess ethanal and

a phenylamine, $C_6H_5NH_2$

b hydroxylamine, NH_2OH

c hydrazine, NH_2NH_2

2 Use the information on page 31 and your understanding of oxidation numbers to deduce the ionic and fully balanced equation for the oxidation of ethanal to ethanoic acid using acidified potassium dichromate(VI).

3 In the presence of NaOH, benzaldehyde, C_6H_5CHO, is both oxidised and reduced. The products are sodium benzoate and phenylmethanol:

$$2C_6H_5CHO + NaOH \rightarrow C_6H_5COO^-Na^+ + C_6H_5CH_2OH$$

Sodium benzoate Phenylmethanol

The mechanism for this reaction is shown below with the curly arrows missing. Copy the mechanism and add the curly arrows to track the movement of the electron pairs in the reaction.

Step 1

Step 2

Step 3