Reducing Carbonyls

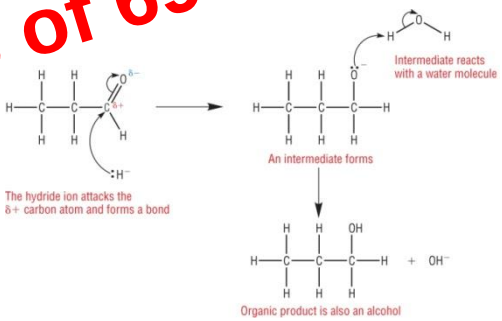
Alcohols can be oxidised to form aldehydes, carboxylic acids and ketones. These carbonyl compounds can then be reduced back into alcohols. The reducing agent used is $NaBH_4$ (sodium tetrahydridoborate/borohydride). In an equation, the symbol [H] is used to indicate that a hydrogen from the reducing agent is reducing the compound.

Aldehyde + 2[H] → Primary alcohol + OH- ion.

The reaction that reduces a carbonyl to an alcohol is a nucleophilic addition. A nucleophile in the form of a H- ion is added onto the carbon chain. The mechanism is as follows:

1. The C=O group is polar, due to the electronegativity of the oxygen atom. This means that the $^{\delta}$+ carbon atom involved in the bond attracts a nucleophile.
2. The H- nucleophile attacks the positive carbon atom and donates its lone pair of electrons. This forms a bond between the carbon and the hydrogen.
3. As the carbon can only have 4 bonds, it breaks one of its bonds with the oxygen atom heterolytically. The electrons involved in this bond are transferred to the oxygen atom, making it a negatively charged ion.
4. The negatively charged oxygen attracts a water molecule in solution. The delta positive hydrogen atoms in the polar water molecules are attracted to the negatively charged oxygen.
5. The oxygen atom donates its lone pair of electrons to the hydrogen atom of the water molecule. The bond between the hydrogen and the oxygen of the water breaks heterolytically and a bond forms between the hydrogen and the oxygen of the carbonyl.

This produces an alcohol and an OH- ion.



Fatty acids and triglycerides

Fatty acids are carboxylic acids. They have long alkyl groups attached to the carboxyl group. Saturated fatty acids don't have any C=C bonds in their carbon chain, whereas unsaturated fatty acids have at least one C=C bond in their carbon chain.

Triglycerides are triesters – they have three ester bonds. They are made up of three fatty acids and one molecule of glycerol (propan-1, 2, 3-triol). The carboxyl groups of the fatty acids and the hydroxyl groups of the glycerol react to form ester bonds. This releases three molecules of water in a condensation reaction.

$3RCOOH + CH_2(OH)CH(OH)CH_2(OH) \rightarrow CH_2COORCHCOORCH_2COOR + 3H_2O$

Naming fatty acids can be done in two ways: systematic and shorthand.

Using the systematic method, the fatty acid is named just as any other carboxylic acid e.g. tetradecanoic acid. If the fatty acid is unsaturated, the carbon atoms the double bond appears on are included and the suffix is changed to –enoic. E.g. if there are C=C bonds on carbons 5, 7 and 12, tetradecanoic acid becomes tetradeca-5, 7, 12-trienoic acid.

Using the shorthand method, only the number of carbons and the double bonds (if any) are detailed. E.g. tetradecanoic acid would become 14, 0 for 14 carbons and 0 double bonds. Tetradeca-5, 7, 12-trienoic acid would become 14, 3 (5, 7, 12) for 14 carbons and 3 double bonds on carbons 5, 7 and 12.

As unsaturated fatty acids possess C=C bonds, they can form cis-trans isomers due to the lack of molecular rotation around the C=C bond. Almost all naturally occurring unsaturated fatty acids form cis isomers, with the hydrogens on the same side of the double bond. This results in bent or curved molecules. Some unsaturated fatty acids form trans fatty acids, as a result of processing, where the hydrogens lie on opposite side of the double bond, forming long, straight molecules. Trans fatty acids have similar shapes to saturated fatty acids.

Trans fatty acids and saturated fatty acids are associated with heart disease due to this long, straight shape. This shape allows them to overlap with one and other and adhere together due to the formation of van der Waal's forces between the molecules. As this happens in the blood vessels, the resultant clumps of fatty acids block arteries and blood flow, leading to an increased risk of CHD. Trans fatty acids also raise the levels of LDL's in the blood and lower the levels of HDL's in the blood.

$NH_2C(CH_3)COOH + NH_2C(CH_3)COOH \rightarrow H_2NC(CH_3)HCONHC(CH_3)HCOOH$ or $HOOCC(CH_3)NHCOC(CH_3)HNH_2$

Polypeptides can be hydrolysed like other polyamides. Heating proteins with HCl for 24 hours is used to hydrolyse them. A shorter reaction time will break the protein into small sequences of amino acids, instead of individual amino acids. This is useful for working out the specific sequence of amino acids in proteins.

Gas Chromatography

Gas chromatography is another method of separating out substances in a mixture. It uses the same principle of TLC but is more accurate and separates different substances more precisely. Gas chromatography is generally used for volatile liquids.

The stationary phase in GC is usually a viscous liquid, such as a long chain alkane, or a solid. In the case of liquid, the liquid is used to coat the inside of a long tube, or it coats beads which are packed into the tube. The tube and beads act as the solid support for the liquid stationary phase.

The mobile phase is an unreactive carrier gas, such as nitrogen, helium or any Group 0 gases.

GC separates out substances in a mixture by using the different levels of solubility/adsorption in each substance. If the stationary phase is a viscous liquid, the different substances in the mixture will have different levels of solubility, and therefore spend different amounts of time dissolved in the stationary phase. Substances with high levels of solubility will spend more time dissolved in the stationary phase and take longer to leave the coil. Substances with lower levels of solubility will spend less time dissolved and more time in the carrier gas, and therefore will spend less time in the coil. If the stationary phase is a solid, then the different substances have different levels of adsorption to the phase, the same as in TLC.

1. The sample is vaporised and injected into the machine, along with the carrier gas.
2. The carrier gas moves through the coil, carrying with it the vaporised sample.
3. Depending on whether the stationary phase is a liquid or a solid, the different substances are separated out by the different levels of solubility/adsorption.
4. Each substance therefore spends a different amount of time in the machine, which gives varying retention times (time taken for the component to pass from the inlet to the detector).
5. The retention times are given on a graph.

The gas chromatogram is a series of peaks that shows the different substances in the mixture. A peak is produced when the detector senses something other than the carrier gas leave the coil. The retention time is read off the graph. The area under each peak can be used to determine the relative proportions of each substance in a mixture. E.g. if the area of one peak is three times greater than the area of another peak, the proportion of that substance is three times greater than that of the other substance.

Each compound has a unique retention time, so the retention times that are obtained from the gas chromatogram can be compared with the retention times of known compounds in order to identify them. However, different conditions (temperature, stationary and mobile phases used) will give different retention times, so the known values must have been obtained using the same conditions.

GC has some limitations. GC is very good at separating substances out in a mixture, but retention time values are not that good for identifying different compounds. This is because many compounds have very similar retention times that are not always easily distinguished on a graph. Also, two different compounds may only give one peak, so these two compounds would not be identified as separate. Another problem is that compounds can only be identified if you have reliable retention times with which to compare your observed retention times. This means that the recorded retention times must have been taken in the same conditions as the observed retention times.

Mass Spectrometry

Mass spectrometry is used to identify compounds. It produces a mass spectrum that is specific to every compound. The compound is vaporised and then bombarded with electrons. This knocks off electrons from atoms in the molecules, ionising it. It also breaks some molecules of the compound into fragments. The molecules become positively charged. The ionised molecules are then accelerated using electric fields and then passed through the spectrometer. This consists of a magnetic field along a curved tube. Ions are deflected according to their charge and mass. Ions with a smaller mass will be deflected more than ions with a larger mass. Ions with a higher charge will be deflected more than ions with a smaller charge. When the ions are deflected, they hit a detector plate, creating a current. The voltage of the current is specific to each ion, which allows them to be identified. This information is reflected on a mass spectrum: a graph with the relative abundance of each ion along the y-axis and the mass/charge ration on the x-axis (the mass divided by the charge, which is usually +1).

The peak at the highest mass/charge ratio is the original compound, so the highest mass/charge value is the molecular mass of the original compound. The other peaks are due to the fragments created by the bombardment of the compound by electrons. Each compound has a unique fragmentation pattern, so two compounds with the same molecular mass and formula will have different mass spectra.

Common fragments:

- $CH_3^+ = 15$
- $CH_2CH_3^+ = 29$
- $CH_2CH_2CH_3^+ = 43$
- $OH^+ = 17$
- $C{=}O^+ = 28$

GC-MS

Combining gas chromatography and mass spectrometry allows mixtures to be separated out and identified more accurately than using either technique in isolation. Gas chromatography separates out substances very efficiently, but using retention times to identify the constituent compounds can give inaccurate data, as different compounds may have the same retention times and retention times must be compared with retention times recorded under the same conditions. Mass spectrometry is very good for identifying compounds, as each compound has a unique mass spectrum, but cannot separate out different compounds.

They are therefore used together. Gas chromatography is used to separate out a substance into its constituent compounds. These compounds then hit a detector at the end of the coil, which is connected to a mass spectrometer. This produces a mass spectrum for the compound.

High performance liquid chromatography is another type of chromatography that is combined with mass spectrometry to separate and identify compounds. In HPLC, the stationary phase is a solid packed into a glass column (e.g. silica beads). The mobile phase is a solvent. The mobile phase and the mixture are pushed through the column at high pressure, which increases the speed of separation.

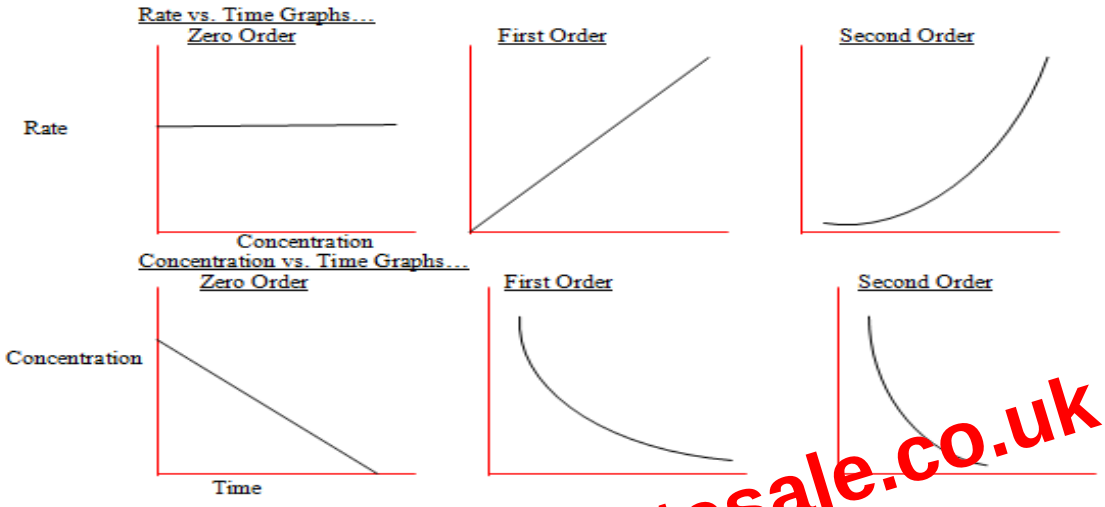
Uses:

- GC-MS is used in forensics, for identifying compounds found at crime scenes, and matching them to compounds (DNA, cloths fibres) collected from suspects.
- Airport security uses GC-MS to test for drugs or explosives. The MS can be programmed to test for a particular substance, which makes the process fast.
- Space probes use GC-MS machines to identify compounds found on extraterrestrial bodies.
- GC-MS is used in environmental analysis to monitor air pollution, water pollution or pesticide levels in food or ecosystem.

Reaction Orders and Half Life

You can work out the order of a reactant by looking at the shape of a rate-concentration graph. A rate concentration graph can be made from a concentration-time graph:

1. Find the reaction rate at different times during the reaction by finding the gradient (tangent method)
2. Record the concentration of the reactant at these points.
3. Plot the reaction rate and concentration for each point in time on a graph to create the rate-concentration graph.



- For 0 order reactants, the conc-time graph is a steady, straight decrease in reactant concentration. For the rate-conc graph, it is a horizontal line.
- For first order reactants, the conc-time graph is a downward curve. For the rate-conc graph, it is a steady increase, as the rate is directly proportional to [X]
- For second order reactants, the conc-time graph is a steep curve downwards. For rate-conc graphs, it is an upward curve, as the rate is proportional to $[X]^2$

Half life is the time taken for the reactant concentration to decrease by half. The half life of a first order reactant is independent of the concentration, so it doesn't matter what the concentration of a reactant is, the half life will always be constant. Therefore, half life can be used to identify the order of a reactant: if the reactant is first order, the half life will be constant.

Acids and Bases

A Bronsted-Lowry acid is a proton donor – it releases protons (H+ ions) into a solution. The H+ ions then react with water to form hydronium ions (H_3O^+). In solution, it is very rare that H+ ions exist as just protons (the concentration of free protons in water is estimated to be 10^{-130} mol dm^{-3}). H+ ions react with water molecules to form hydronium ions. The water molecules have two lone pairs of electrons, which can accept the H+ ion to form a dative covalent bond

A Bronsted-Lowry base is a proton acceptor – it accepts H+ ions in solution. When mixed with water, they accept H+ ions from water, forming OH- ions and a positive ion.

Reactions of acids:

- Acids react with metals to form a metal salt and hydrogen. The metal donates electrons to the H+ ions. The metals are oxidised and the H+ ions are reduced, forming a salt.

  $2HCl + 2Na \rightarrow 2NaCl + H_2$.

  $2H+ + 2Na \rightarrow 2Na+ + H_2$
- Acids react with carbonates to form a salt, carbon dioxide and water. The ions reacting in this reaction are the H+ ions and the carbonate ions
- Acids react with metal hydroxide and oxides (which are bases) to form a salt and water. The ions reacting in this reaction are the OH- ions or the O^{2-} ions, depending on whether the base is a metal hydroxide or a metal oxide.

Acids dissociate in water to release H+ ions and spectator ions (Cl^-, SO_4^{2-} etc). Strong acids completely dissociate, meaning that nearly all of their H+ ions are released. Strong bases also completely ionise, meaning that nearly all of the OH^-/O^{2-} ions are released. Weak acids only partially dissociate, meaning that only some of their H+ ions are released. Weak bases also only partially dissociate. This is why strong acids produce more acidic solutions – they release more H+ ions into the solution than weaker acids, as they dissociate completely, which lowers the pH. The same goes for strong bases.

Acids can be mono-, di-, or tribasic. This means that different acids have different numbers of protons and therefore dissociate to release different numbers of protons.

Monobasic acids release one proton: $HCl \rightarrow H^+ + Cl^-$

Dibasic acids have two protons and release H+ ions in two stages:

$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$

$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$

Tribasic acids have three protons and release them in three stages:

$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$

$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$

$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$

E.g. a standard hydrogen half cell is used to determine the electrode potential of a half cell. A hydrogen half cell is set up by bubbling a hydrogen gas into a solution of H+ ions. A platinum electrode is used to facilitate the transfer of electrons. An equilibrium is set up between the hydrogen and the H+ ions: $2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2\,(g)}$. When testing the electrode potential of a half cell, the conditions must be constant, as the position of equilibrium in each reaction is affected b y temperature, pressure and concentrations. The standard conditions for a standard hydrogen electrode potential are:

- Both solutions (hydrogen and the other half cell) must be 1 mol dm^{-3}
- Pressure must be 100kPa
- Temperature must be 298 K

The standard electrode potential is the voltage produced by a half cell when compared to a standard hydrogen half cell. The voltage produced by a standard hydrogen half cell is 0 V. To measure the standard electrode potential, a half cell is connected to a hydrogen half cell and the voltage produced is measured.

The cell potential is the difference in voltage between the electrode potentials of the two half cells. The cell potential shows the total voltage produced by the electrochemical cell.

Cell potential = electrode potential of the reduced element – electrode potential of oxidised element

Isomerism in Complex Ions

Complex ions can show optical isomerism and E/Z isomerism. For a complex ion to show optical isomerism it must comprise be one of three types:

- A metal ion with three bidentate ligands attached, to have an overall coordinate number of 6. E.g. $[Ni(en)_3]^{2+}$.
- A metal ion with two bidentate ligands attached and two monodentate ligands attached, forming an overall coordinate number of 6. E.g. $[Fe(en)_2Cl_2]$.
- A metal ion with one hexadentate ligand, forming an overall coordinate number of 6. E.g. $[Cu(EDTA)]^{2-}$

The optical isomers formed will be non-superimposable mirror images of each other. They will both rotate plane polarised light, but in opposite directions. An equal mixture of both isomers will be optically active as they will both rotate the plane polarised light in opposite directions, cancelling each other out.

Complex ion also exhibit cis-trans isomerism. Complex ions with four monodentate ligands, with two identical pairs of ligands can be cis or trans isomers, depending on which side of the metal ion the two ligands are on. If the two identical ligands are on opposite sides of the metal ion, the complex ion is a trans isomer. If they are on the same side of the metal ion as each other, then it is a cis isomer.

Cis-platin is a complex comprised of a platinum(II) ion bonded to two chloride ligands and two ammonia ligands in a square planar shape. Cis-platin is where the chloride and ammonia ligands are on the same sides of the platinum ion. Cis-platin is used in chemotherapy to slow and stow the growth of cancer cells. Cis-platin enters cells and easily releases its chloride ligands, allowing it to form coordinate bonds with the lone pairs of nitrogen atoms in the nitrogenous bases of DNA. This prevents DNA from replicating and therefore the cell cannot divide. This works for all cells but has a much greater effect on cancer cell than normal body cells as they divide at a much faster rate than normal body cells. However, fast dividing body cells, such as hair cells and the cells that make up the stomach lining, are also affected, which accounts for the hair loss and nausea experienced during chemotherapy.

Octahedral complexes with a 4 ligands of one type and 2 ligands of another type (e.g. $[Ni(H_2O)_4Cl_2]$) can also show cis-trans isomerism. If the two odd ligands are opposite each other (on either side of the metal ion) it is a trans isomer. If they are next to each other (adjacent) then it is a cis isomer.

Redox Reactions in Experimental Chemistry

As transition metals have variable oxidation states, they can gain and lose electrons easily. This makes them good oxidising and reducing agents.

Acidified potassium manganate solution ($KMnO_4$) is used as an oxidising agent as the Mn^{7+} in the manganate compound is reduced to an Mn^{2+} ion. It therefore donates electrons to help other species become reduced. When the Mn^{2+} ion is released into the solution, it forms a manganese-aqua complex ($[Mn(H_2O)_6]^{2+}$). The MnO_4^- ion is purple and the $[Mn(H_2O)_6]^{2+}$ is colourless, so when the reaction takes place, there is a colour change from purple to colourless.

E.g. MnO_4^- ions oxidise Fe^{2+} ions in a redox reaction: $MnO_4^- + 8H^+ + 5Fe^- \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

Acidified potassium dichromate is another oxidising agent. It contains dichromate ions ($Cr_2O_7^{2-}$) which can oxidise a reducing agent in a redox reaction. The Cr^{6+} ions are reduced to Cr^{3+} ions in the reaction.

E.g. $Cr_2O_7^{2-}$ oxidise zinc in a redox reaction: $Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$

When the Cr^{3+} ions are released in solution, they form a chromium-aqua complex, which is green. As the dichromate ions are orange, the colour change that occurs is orange to green. This is the same as when potassium dichromate is used to oxidise alcohols.

Oxidising agents and reducing agents such as these are used in redox titrations. These are done to find out the exact quantity of oxidising agent needed react with a known quantity of reducing agent, or vice versa. It is done is the same way as an acid-base titration, but with a few differences.

1. A known quantity of reducing agent is added to a conical flask. E.g. Fe^{2+} ions.
2. Excess dilute sulphuric acid is added to the flask. This is the acidification, and is done so that there are enough H^+ ions for the oxidising agent to be reduced.
3. Oxidising agent is then slowly added, in 1 cm^{-3} increments, using a burette.
4. A colour change should occur when the end point is reached and all the reducing agent has reacted with the oxidising agent.
5. Mark the final volume of oxidising agent used. This is the rough titration.
6. Repeat the titration. When the oxidising agent volume used in the first titration is approached, add the oxidising agent drop by drop until a colour change is seen.

An example of a colour change is when $KmnO_4$ is used. MnO_4^- ions are purple in solution, and the reducing agent will either be colourless or coloured. The end point of the reaction is when the solution turns purple, as it this point all of the reducing agent will have reacted and there will be nothing less to remove the MnO_4^- ions from the solution.