Organic and Biological Chemistry

Production of ethanol

Ethanol is usually produced by fermentation of glucose (a monosaccharide). In cases where glucose is not initially present it can be obtained by hydrolysis (reaction with water) of more complex carbohydrates (polysaccharides and disaccharides) sometimes referred to as starches.

Hydrolysis of a polysaccharide to a disaccharide $2(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_{12}H_{22}O_{11}$

Hydrolysis of a disaccharide to a monosaccharide $C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$

Fermentation of a monosaccharide $C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$

The optimum temperature for fermentation is between 20°C and 30°C since this is the range in which the enzymes in the yeast cells (which catalyse the reaction) are effective. Fermentation is exothermic and must be cooled to maintain this temperature range.

Fermentation is anaerobic and although a small amount of oxygen allows yeast cells to grow, excess oxygen can oxidise ethanol to ethanoic acid (vinegar).

Primary, secondary and tertiary alcohols

A hydroxyl (OH) group is in the following position if it is bonded to a carbon which is bonded to:

	In terms of hydrogens	In terms of alkyl groups	
primary two or more hydrogens one o		one or no alkyl groups	
secondary one hydrogen two alkyls group		two alkyls groups	
tertiary	no hydrogens	three alkyl groups	

Primary and secondary alcohols can be distinguished from tertiary alcohols by reaction with acidified dichromate solution.

When a reaction occurs (a primary or secondary alcohol is present) the dichromate is reduced to chromium (III) and therefore will change colour from **orange** to **green**. This reaction is slow at room temperature.

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

dichromate ions (orange) chromium ions (green)



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Primary alcohols will be oxidised first to an aldehyde,



propan-2-ol

Tertiary alcohols will not react with acidified dichromate.

Aldehydes and Ketones

Aldehydes are produced by oxidation of primary alcohols but are readily oxidised to a carboxylic acid so must be distilled off from the reaction mixture as they are formed. This can be achieved practically if the oxidising agent is added to an already heated mixture since the boiling point of the aldehyde will be the lowest in the mixture and therefore be distilled off as it forms.

Aldehydes can be heated with an acidified oxidising agent to form carboxylic acids or heated in an alkaline solution of an oxidising agent to form carboxylate ions.

Ketones are produced by oxidation of secondary alcohols. Heating is required to increase the rate of reaction.

Ketones cannot readily be oxidised. This difference in properties can be used to distinguish aldehydes from ketones.

For example, if the substance is known to be either an aldehyde or a ketone, then it can be placed in an acidified dichromate solution or a solution of ammoniacal silver nitrate (Tollens' reagent).

Tollens' reagent is a mild oxidising agent. It cannot oxidise alcohols, but it can oxidise aldehydes because aldehydes are easily oxidised to carboxylate anions.

	Aldehyde	Ketone
Acidified dichromate (orange)	Aldehyde reacts to form a carboxylic acid. Solution will turn green.	No reaction, solution stays orange.
Tollens' reagant	Aldehyde reacts to form a carboxylate anion. A 'silver mirror' forms.	No reaction.

Carboxylic Acids

Carboxylic acids can be produced by the oxidation of aldehydes or primary alcohols (see above for more details).

Carboxylic acids are weak acids and ionise to a small extent in water, for example:

$$CH_3-C_{OH}^{0} \iff CH_3-C_{O^-}^{0} + H^+$$

Carboxylic acids react with bases to form ionic carboxylate salts. The reactions are exothermic and occur quickly.

If the carboxylic acid is insoluble it will appear to dissolve as it reacts.

If the base is a carbonate or hydrogencarbonate, effervescence of carbon dioxide gas will occur.

The salts of sodium and potassium carboxylates are soluble in water because of the ion-dipole attraction between the ions and water.

For this reason drugs which contain carboxyl groups are often taken in the form of carboxylate salts. Specifically, the carboxylic acid form is combined with sodium hydrogencarbonate as a solid tablet. When combined with water the carboxylic acid form reacts with the hydogencarbonate anion and is converted to a water-soluble carboxylate form (carbon dioxide effervescence occurs also). The carboxylate ion is therefore able to be distributed through the stomach, where is is converted back into molecular (carboxylic acid) form by the hydrochloric acid in the stomach.

Amines

An amine group can be classed as primary, secondary or tertiary depending on the number of alkyl groups surrounding the nitrogen. Ammonia is included for comparison.

Classification	Number of hydrogens	Number of alkyl groups	
Ammonia	3	0	
Primary amine	2	1	
Secondary amine	1	2	
Tertiary amine	0	3	

Since there is an unbonded pair of electrons on an amine, a hydrogen ion (proton) can be accepted, forming a 'substituted' ammonium ion (an ammonium ion NH_4^+ with one or more alkyl groups instead of hydrogens). In this way an amine can act like a base (proton acceptor). The substituted ammonium form is also called the protonated form of the amine.



The <u>salts</u> of amines (ionic compounds in which the substituted ammonium ion is the cation) are soluble in water because of the ion-dipole attraction between the ions and water. An <u>amine</u> (i.e. not the salt) is not soluble in water because hydrogen bonds, though strong enough to attract to the water, are not strong enough to form ion-dipole bonds (break apart the ions in the amine).

For this reason, drugs with amine groups are usually taken in the form of their salts (i.e. in ionic form).

Esters

Ester production

An ester can be produced by a *condensation* reaction between an alcohol and a carboxylic acid. The other product formed is water.



The production of an ester from the reaction of an alcohol and a carboxylic acid is slow at 25°C. An extended period of heating is therefore required to achieve a satisfactory yield of ester. The

process used is called *reflux*, where the reactants and products repeatedly boil and pass into a condenser as vapour, where they condense and return to the liquid mixture.



A trace of concentrated sulfuric acid is present during the process as a catalyst.

Hydrolysis of esters

Esters may be refluxed with an acidic or alkaline solution (i.e. aqueous acid or base) to undergo *hydrolysis*. One of the products is an alcohol.

Conditions	Other reactant	Other product
Acidic (H ⁺ is a catalyst)	water (H ₂ O)	Carboxylic acid
Alkaline	hydroxide ions (OH ⁻)	Carboxylate ion

Note that a strong acid can be added to carboxylate ion form to produce the carboxylic acid form.

Amides

The products of a condensation reaction between an amine and a carboxylic acid are water and an amide. The water forms from the -OH on the acid and a H from the amine. This reaction is usually refluxed.

Hydrolysis of an amide requires extended refluxing under strongly acidic or alkaline conditions.

Conditions	Products
Acidic (reaction with hydronium ions)	carboxylic acid, substituted ammonium salt or ammonium
Alkaline (reaction with hydroxide ions)	carboxylate salt, amine or ammonia

Proteins

Proteins are polymers, long chains with repeating units. The monomers (single units) that react to form proteins are called amino acids, because they have an amine group at one end and carboxylic acid at the other end, as shown below. Only the side groups (labelled R below) change.



General formula of an amino acid (where R is any organic structure)

Amino acids are able to self-ionise. The carboxylic acid on one molecule can donate a proton, and the amine group on another group can accept it. The self-ionised form of an amino acid is called a 'zwitterion'.



Self-ionised form of an amino acid (zwitterion)

Many amino acids reacted together form a protein. The amine group in one molecule reacts (by a condensation reaction) with the carboxylic acid group in another molecule, forming an amide link. In proteins, amide links are called 'peptide links'.



Highly polar covalent bonds present in the protein such as O-H and N-H allow hydrogen bonding between the chain and water, or between two different sections of the protein chain (since the chain is long enough to fold over many times).

All proteins are folded into a complex spatial (3D) arrangement, with parts of the chain attracted to other parts by specific secondary forces such as hydrogen bonding. This complex arrangement serves a specific purpose such as providing sites where a particular biological function can be performed. Changes to the pH or temperature disrupt the attractions between sections of protein chain.

For example increased pH changes carboxyl groups to carboxylate groups, and decreased pH changes amine groups to substituted ammonium ion groups; either of these will cause them to be attracted by ion-dipole forces instead of hydrogen bonding. Increased temperature will cause vibrations which break the interactions between chain sections. Any of these changes will permanently alter the spatial arrangement (it can't reform when the conditions change back) so the protein can no longer perform its function.

Triglycerides

Triglycerides are triesters, formed by reaction of fatty acids (carboxylic acids with long unbranched non-polar tails) of propane-1,2,3-triol.

$CH_2 - OH$	HOOC(CH ₂) ₆ CHCH(CH ₂) ₆ CH ₃	CH ₂ OOC(CH ₂) ₆ CHCH(CH ₂) ₆ CH ₃
CH – OH +	HOOC(CH ₂) ₁₄ CH ₃	$CHOOC(CH_2)_{14}CH_3 + 3H_2O$
$CH_2 - OH$	HOOC(CH ₂) ₄ CHCH(CH ₂) ₅ CH ₃	CHOOC(CH ₂) ₄ CHCH(CH ₂) ₅ CH ₃
propan-1,2,3,-triol (glycerol)	3 fatty acids (could be the same or different)	triglyceride (triester)

The likely state of a triglyceride at room temperature depends on the degree of unsaturation (alkene groups) present in the molecule. Less alkene groups means the chains can pack more closely together, so the dispersion forces are stronger and the triglyceride is more likely to be a solid (rather than liquid) at room temperature.

	Alkene groups	Likely state (at room temperature)	Likely source	Common name
Unsaturated	More	Liquid	Plants or fish	Oil
Saturated	None	Solid	Land animals	Fat

The degree of unsaturation can be measured using a solution of iodine or bromine. Both iodine and bromine solutions have a visible brown/orange colour; therefore when they react by addition with alkene groups, this colour disappears. So if iodine or bromine solution is slowly added to the triglyceride, the colour staying will indicate the alkene groups have been used up. The measure of moles of iodine or bromine added can be used to calculate the moles of alkene groups present.



The level of unsaturation of a triglyceride can be decreased by addition of hydrogen. This increases the melting point of the triglyceride. This process is called 'hydrogenation', and requires high pressure, high temperature and presence of a catalyst such as nickel in order to increase the rate of reaction.

Carbohydrates

Carbohydrates are naturally occurring sugars and their polymers. They usually have the general formula $C_r H_{2\nu} O_{\nu}$ which can also be written $C_r (H_2 O)_{\nu}$, hence 'carbo' 'hydrates'.

They are defined more precisely as either polyhydroxy aldehydes or polyhydroxy ketones, or their polymers. The prefix "hydroxy-" shows the presence of a hydroxyl functional group (-OH).

Carbohydrates can be classified as monosaccharides, disaccharides, or polysaccharides.

<u>Monosaccharides</u> can exist in both a ring and chain form (an equilibrium of both structures). In the chain form a monosaccharide has either an aldehyde or a ketone functional group, whereas in the ring form it will have neither.

Glucose is a monosaccharide that has an aldehyde in its chain form. For this reason the chain form of glucose will react with Tollen's Reagent to form a silver mirror (its ring form will not).

<u>Disaccharides</u> are produced by condensation reactions (water is the other product) between two ring form monosaccharides. Disaccharides can undergo hydrolysis to break down into monosaccharides.

Polysaccharides are formed by condensation reactions of multiple monosaccharides.

 $-OH + HO \rightarrow -O - + H_2O$

Simpler carbohydrates (low numbers of carbons) tend to be soluble in water (due to the amount of polar hydroxyl groups). As the molecules become more complex (e.g. polysaccharides), they become insoluble in water since they have less hydroxyl groups compared to the number of carbons.