

Year 2, Organic Chemistry, Chapter 18:

Expanded version of last year's Chapter on Alcohols

You will be tested on it this year, so I have reprinted it for you. (Please re-read ALL the First Year Chapters.)

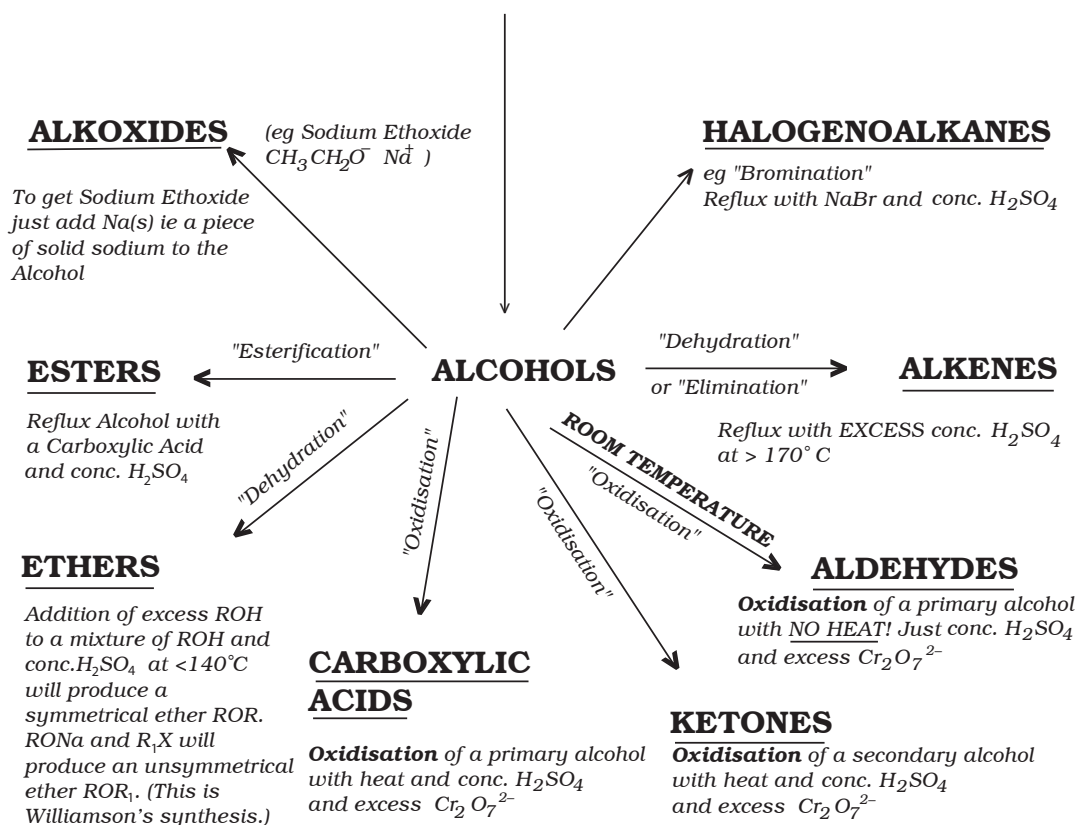
- An **Alcohol** is **any** organic molecule that contains an hydroxy (“–OH”) group that is connected to a C atom in the molecule. However, if that C atom also has a double-bonded O atom connected to it, “>C=O” (and this is what forms a Carbonyl group), then the molecule is not an Alcohol and instead it is an **acid**.
- The location of the hydroxy group must be identified in the name of the Alcohol, and if there are two hydroxy groups, then both their locations must be identified in the “.....diol”, and if there are three hydroxy groups, then the three locations must be identified in the “.....triol”, and so on.
- Alcohols have an O atom bonded to an H atom (“R.C–OH”), therefore **all Alcohols have inter-molecular Hydrogen bonds** which give them higher boiling points than they would have had if they had had only vdW inter-molecular forces of attraction.
- Since Alcohols are hydrogen bonded, they are less volatile and they have higher boiling points than alkanes with the same (or similar) molecular mass.
- All Alcohols have inter-molecular hydrogen bonds, and water is also hydrogen bonded – therefore **Alcohols are soluble** (to differing extents) **in water**. [For Alcohols containing a given number of ‘–OH’ species, the larger the number of C atoms in the Alcohol, the less soluble it will be.]
- Alcohols for human consumption are made by “fermentation”, but Alcohols for industrial purposes are often made by reacting alkenes with steam using H_3PO_4 as the catalyst.
- Oxygen is the second most electronegative element known to man, therefore the O atom in an Alcohol will draw the electron cloud density from the C atom towards itself thus causing the O atom to become O^{\ominus} and the C atom to become C^{\oplus} . The resulting C^{\oplus} will be attractive to any nucleophile, and Alcohols will thus be subject to **nucleophilic** reactions.
- Alcohols can be classified according to the number of C atoms that are attached **to the C atom to which the hydroxy (“–OH”) group is attached**. According to this method of classification, Alcohols will be **primary/ secondary/or tertiary Alcohols** – and the reactions of each of these Alcohols will differ from each other.
- For ‘A’ Level purposes, only two groups of reactions need to be learnt for Alkanes [i.e. (i) Combustion, and (ii) Halogenation by Free Radical Substitution], and for Alkenes only one group of reactions needs to be known (i.e. electrophilic addition reactions); but, for Alcohols **many** reactions need to be known – but the examiners ask more questions about the Oxidisation of Alcohols than they do about any other group of reactions. **It is absolutely vital to know these reactions by heart** (and also to know the colour changes that are involved) otherwise you will just lose masses of valuable time trying to remember things in the exams.
- It is also important to be able to recognise the infra-red spectrum graphs (spectrographs) for Alcohols/Acids/ Ketones/and Aldehydes – but luckily these are all easy to recognise.
- The last bit of knowledge required is the importance of the use of Alcohols as a fuel in those countries that do not possess any underground oil fields but that do possess vegetables/plants (such as sugar cane in Brazil)/ fruit/etc that can be converted easily and cheaply into Alcohols. However, using land to grow fuel for cars is of questionable social value because it **raises the cost of food for human beings and animals!** Why should cars be more important than human beings or animals?
- Alcohol loosens the inhibitions of human beings and this makes them feel “relaxed”. However, this also reduces their self-control and makes them do things that they would otherwise not do (when they were sober) e.g. **to kill another human being when driving under the influence of drink is one of the most IRRESPONSIBLE, WICKED and GROSSLY STUPID acts known to man.**

Required reactions involving Alcohols for 'A' Level purposes

(page 13 onwards shows many of these reactions in greater detail)

AS Level methods of obtaining an alcohol

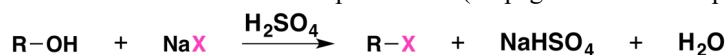
- 1) "Fermentation" of a sugar with yeast (as the catalyst).
- 2) "Hydration" of an alkene with steam (by electrophilic addition).
- 3) "Hydrolysis" of a halogenoalkane.



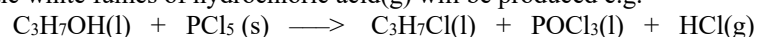
NB1 The **dichromate ion** is conventionally supplied by either Sodium or Potassium Dichromate. Please remember that Potassium Dichromate is carcinogenic. It is my understanding that the Cr^{6+} ion is quickly transformed into the Cr^{5+} ion and it is *that* which is corrosive and dangerous. **Do make sure that you dispose of your reactants appropriately!**

NB2 The **Dehydration Reactions of Alcohols** result in their conversion into alkenes, and involves the elimination of a molecule of water. Dehydration requires the presence of an acid as the catalyst and the application of heat. When transforming an Alcohol into an Alkene, there must be an excess of **CONCENTRATED Sulphuric Acid!** If an excess of the **Alcohol** is used, then an **ether** will be produced. To transform the Alcohol into an Alkene, the temperature must be at least 170°C .

NB3 **Halogenation of an Alcohol:** Alcohols react with strongly acidic hydrogen halides viz. HCl and HBr , and HI (but the reaction of a primary Alcohol and HCl(aq) is **very slow** at RTP). **Alcohols do NOT react with nonacidic NaCl , NaBr , or NaI .** Chemistry LibreTexts (written by Jim Clark) points out that primary and secondary Alcohols can be converted to alkyl chlorides and bromides by allowing them to react with a mixture of a sodium halide and concentrated sulphuric acid (cf. page 12 of this Chapter).



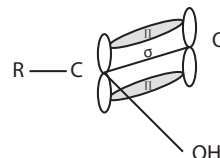
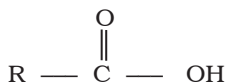
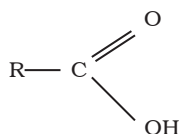
NB4 One of the classic tests for an Alcohol is to react it with phosphorous pentachloride, PCl_5 , whereupon the characteristic white fumes of hydrochloric acid(g) will be produced e.g.



Before starting this Section of the Module, I should like to introduce you to a number of new things, and also to remind you about some old things.

1) What is an Alcohol?

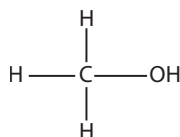
- An Alcohol is a Carbon molecule that contains one or more “-OH” (“Hydroxy”) groups. The Carbon atom to which an hydroxy group is attached CANNOT be part of a Carbonyl Group¹ (“>C=O”), otherwise an Acid would then exist – for example, it can be seen below that the presence of the Carbonyl Group in the diagrams below indicates that the molecule is **NOT an Alcohol** but it is in fact an acid.



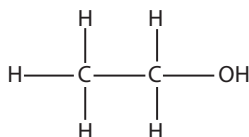
2) The naming of Alcohols

- Start by finding the longest chain of C atoms (just as with an alkane). Now name it so that the ‘-OH’ species has the lowest number. The names of Alcohols must also reflect the number of hydroxy groups that the molecule contains, and the name must state where the hydroxy groups are located. [The naming conventions are the same as those that we have already learnt for other Functional Groups.] *I have drawn and named some Alcohols for you below. These substances may or may not exist in reality. All that I am trying to do is to show you how to name them.*

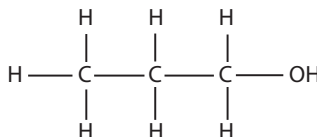
Methanol
CH₃OH



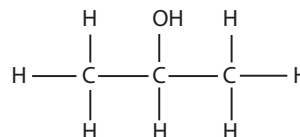
Ethanol
CH₃CH₂OH



Propan-1-ol
C₂H₅CH₂OH

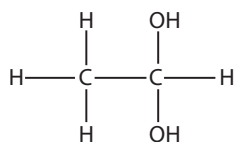


Propan-2-ol
CH₃CHOHCH₃

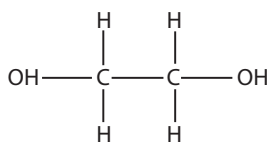


NB There is no such name as Propan-3-ol. Can you work out why this is so?

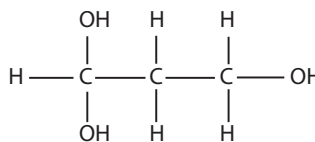
Ethan-1,1-diol
or 1,1-ethanediol²
CH₃CH(OH)₂



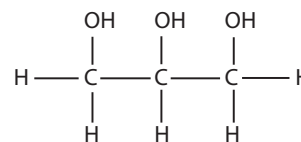
Ethan-1,2-diol
or 1,2-ethanediol
CH₂OHCH₂OH



Propan-1,1,3-triol
or 1,1,3-propanetriol
CH(OH)₂CH₂CH₂OH



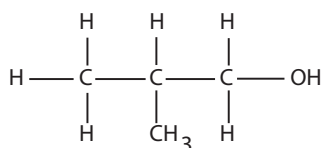
Propan-1,2,3-triol
or 1,2,3-propanetriol
CH₂OHCHOHCH₂OH



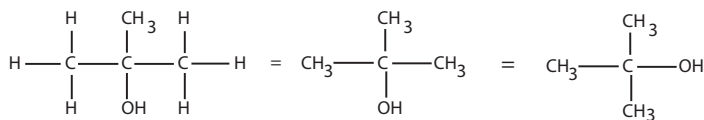
¹ A Carbonyl Group in an organic molecule consists of an O atom double bonded to a C atom.

² American chemists tend to favour this method of naming. Try and keep an open mind about everything in life. Use “the best” that you can find and not just the one that you are used to.

2-methyl propan-1-ol
CH3CH(CH3)CH2OH



2-methyl propan-2-ol
CH3C(OH)(CH3)CH3 or C(CH3)3(OH)



I hope that you can see that the three molecules on the Right are all exactly the same!

3) Electronegativity of the O atom/Partial separation of charge in an Alcohol

- Oxygen is the second most electronegative element known to man; and, since an Alcohol is created by an “Hydroxy” group being attached to a C atom (C–OH), the consequence is that the O atom attracts electron density off all the C and the H atoms and becomes “ δ^- ” and **BOTH** the H atom (in the Hydroxy group) AND the C atom become “ δ^+ ”.
- A “cation” is a positively charged ion and an “anion” is a negatively charged ion, and the C atom to which an hydroxy group is attached (and which has thus become a $\text{C}^{\delta+}$ species) is called a “carbocation” – which is short for a “Carbon-cation”. *Actually, strictly speaking, it should **NOT** be called a carbocation because it is **not** an ION, since it has merely a partial separation of charge in it (i.e. a “ δ^+ ”) and it does **NOT** have a full positive “+” charge! However, that is what it is called, so don’t waste time fighting that battle!³*
- A “carbocation” is thus an **ELECTROPHILE** i.e. it is an **electron pair acceptor** (remember, “phil-” is derived from the Ancient Greek word for “to love” phileo therefore an electrophile is a lover of electrons), and an electrophile will attract and react with **NUCLEOPHILES** i.e. with electron pair donors.

4) Hydrogen Bonding in an Alcohol

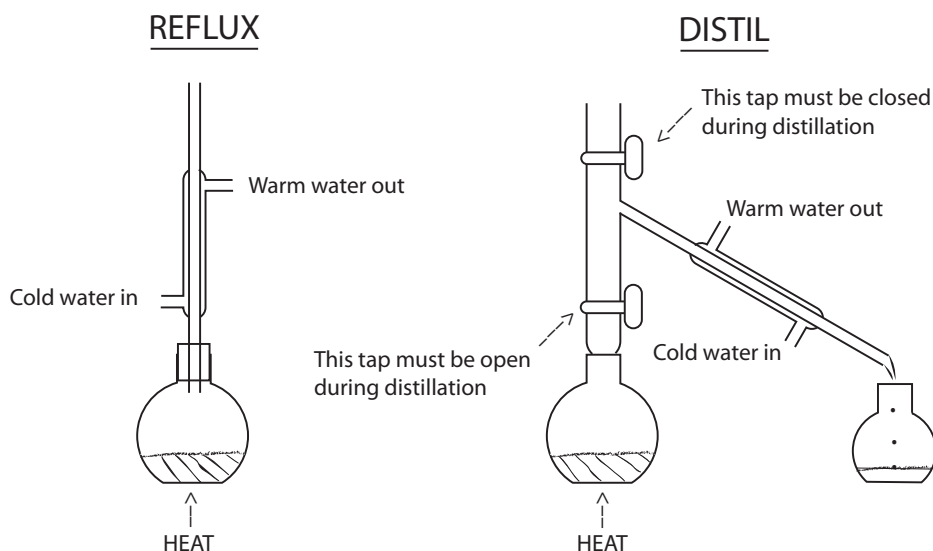
- All Alcohols are Hydrogen bonded, and the larger the number of hydroxy groups in the Alcohol, the greater will be the number of Hydrogen bonds connecting one molecule to a neighbouring molecule – and the more Hydrogen bonds that there are in a substance, the more will the molecules stick together (and the less volatile will the substance be) and the higher will its boiling point be (more about this on page 6).

5) The difference between “Distil” and Reflux”

- Distillation** : When you separate two (or more) mixed liquids by distillation, you heat the mixture until the liquid with the lower (or the lowest) boiling point starts to boil – and it would not matter how much heat you then put into the mixed liquids, **the temperature would remain at the boiling point of the liquid with the lower/the lowest boiling point until all that liquid had boiled off**. *The diagram on the right on the next page shows you how to cool/condense/and collect the substance that has boiled off.*
- Reflux** : In contrast, in “Refluxing”, **the vapour of the liquid that is boiling off is cooled/condensed/and RETURNED to the mixture**. It is not allowed to escape from the mixture! The reason for this is that for certain reactants to react, they may need to be heated with each other for a fairly LONG PERIOD OF TIME (say for one hour) *so that all the reactant molecules have a chance to collide with each other with sufficient energy, and thus react with each other*. However, if the reactants were allowed to separate (by distillation) before they had collided with sufficient energy, then only a small proportion of the reactants would react, and in order to prevent the liquid with the lowest boiling point from being distilled off, **its gaseous vapour must be condensed and returned to the mixture continuously** so that ALL the reactants can react. This process is called *refluxing*.

³ In life it is important to know which battles to fight and which ones you cannot win.

- In Refluxing, a stopper must NOT be placed in the reflux tube otherwise there WILL be an explosion and you will be showered with fragments of broken glass and scarred and possibly even blinded!



- It is however important to understand that in refluxing, *the TEMPERATURE of the reactants will never rise above the boiling point of the liquid with the lowest boiling point*, because whatever heat is injected into the mixture will be used to convert that liquid into a gas. As the gas is then condensed and returned to the mixture, the gas will give up its energy to the cold water in the water jacket. The temperature in a reflux operation will thus always be set by the boiling point of the liquid with the lowest boiling point in the mixture.
- If you wanted to achieve a higher temperature (and thus give the colliding reactant molecules much more energy), then the only way of doing so would be to heat the reactants in a chemical “bomb”⁴ this being a metal canister with very thick walls that are capable of withstanding very high pressures when heated (usually in an oven) – and for some reactions it will be necessary to use a “bomb”, but because the process is dangerous, your teacher will NOT allow you to do that at school (but you will be allowed to do so when you get to University). [*Heating in a “bomb” is required knowledge for one of the reactions of a Halogenoalkane – even though you will NOT be allowed to carry out the experiment in your school lab.*]

6) Protonation

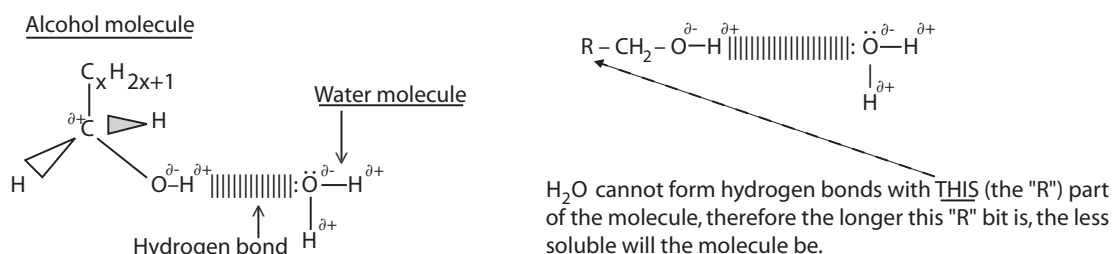
- Protonation is Chemistry English for “Proton donation” – and it is the situation that exists when the species under consideration has had a proton donated to it. *The name therefore is misleading, and it should really be called “proton acceptance” because it is the acceptance for example by an O atom (via its lone pair of electrons) of a proton (i.e. an H⁺ species) that is at issue.* However, this is another of the battles you cannot win, so do not waste time fighting it.

OK, let’s start the Syllabus!

⁴ I personally do not like violence, therefore I do not like the name “bomb”, and I would prefer it if the name were changed to “high pressure containment vessel”.

A1 The Water solubility of Alcohols

- When a substance (X) dissolves in Water, what happens is that each charged or partially charged species of X is surrounded by and forms very weak bonds with water molecules and it is thereby gradually separated away from the main body of X. This process continues until each and every charged or partially charged species inside X is dislodged from the main body of X and is totally surrounded by water molecules – and a homogeneous mixture of charged particles of X surrounded by water molecules is thus obtained.
- You will remember from the Foundation Module that Water molecules are partially polarised and that something will thus dissolve in Water only (i) if it is itself **fully polarised** i.e. if it is an *ionic* substance, or (ii) if it is **partially polarised** i.e. if it is a molecular substance that has a *partial separation of charge in it* (i.e. where there are areas of δ^+ and δ^- in each of its molecules).
- As it happens, both Water and Alcohols are Hydrogen bonded, therefore when an Alcohol is dissolved in Water, then the Alcohol also becomes Hydrogen bonded to the Water molecules.
- However, (for any given number of hydroxy groups in an Alcohol), the longer the Carbon chain the more there will be of the Alcohol that **cannot** form Hydrogen bonds with the water molecules, and the more difficult will it become for the water to dissolve the Alcohol – and thus the less soluble will that Alcohol be.



- The longer the Carbon chain (in say a single hydroxy Alcohol), then the less soluble will the substance be.

Single hydroxy Alcohol	Formula	Approximate Solubility (g of Alcohol per 100g of water)
• Methanol	CH ₃ OH	Very large but not infinite ⁵
• Ethanol	C ₂ H ₅ OH	Very large but not infinite
• Propan-1-ol	C ₃ H ₇ OH	Very large but not infinite
• Butan-1-ol	C ₄ H ₉ OH	8
• Pentan-1-ol	C ₅ H ₁₁ OH	3
• Hexan-1-ol	C ₆ H ₁₃ OH	< 1
• Heptan-1-ol	C ₇ H ₁₅ OH	very low solubility

⁵ Some people use the word "Infinite" here, but there can be no such thing as "Infinity" in the Physical Sciences. If the number of entities in something is **capable of being counted, then it is finite**. The fact that an amount may be too large for Man to count, or that Man does not know where something ends, does not mean that it has no end. "Infinity" can, strictly speaking, be applied only to immaterial things – and it was a concept invented by Primitive Man to indicate that something was **very** large, and the concept was then taken up by theologians to try to describe the concept of "God". Infinity has very little part to play in Science **other than in Mathematics**. Always try to use your brains to test the things that you hear. For example, if you hear that there is an infinite number of molecules of water in the oceans and the seas of the world, then (since each mole of water molecules has a known mass) it would be the case that the oceans and the seas of the world would have an infinite mass! *OK, do they? Well, in that case, there is not an infinite number of molecules of water in the earth's seas and oceans!* The process of logic whereby a truth can be established by carrying an **incorrect** assumption to its logically absurd conclusion is called a '**reductio ad absurdum**'.

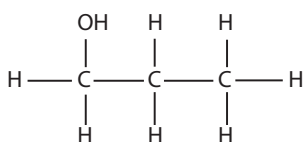
A2 The Volatility and Boiling Points of Alcohols

- Alcohols have modestly strong inter-molecular Hydrogen “bonds”, and they are therefore less volatile and have higher boiling points than liquids with the same molecular mass but which have no Hydrogen bonds.
- The greater the molecular mass of the molecules of a substance, **the larger the number of electrons that there will be in each molecule**, therefore the greater will be the inter-molecular force of attraction between neighbouring molecules, and the more will they hold on to each other.⁶ Therefore for any given number of hydroxy groups inside an Alcohol, the boiling point of such an Alcohol will rise as the molecular mass increases e.g.

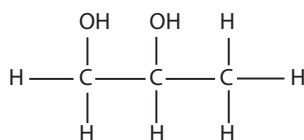
For SINGLE hydroxy Alcohols	Formula	Approximate Boiling Point in °C (Source Stark & Wallace : ISBN 0-7195-3951-X)
• Methanol	CH ₃ OH	64.5
• Ethanol	C ₂ H ₅ OH	78.5
• Propan-1-ol	C ₃ H ₇ OH	97.2
• Butan-1-ol	C ₄ H ₉ OH	117
• Pentan-1-ol	C ₅ H ₁₁ OH	138
• Hexan-1-ol	C ₆ H ₁₃ OH	157
• Heptan-1-ol	C ₇ H ₁₅ OH	205

- However, the more hydroxy groups that there are in an Alcohol, the greater will be the Hydrogen bond force of attraction between the molecules of such an Alcohol, and the less volatile will it be (compared to an Alcohol with the same number of C atoms but with fewer hydroxy groups). Could you now spend a few seconds thinking about the inter-molecular forces of attraction between the following three substances, and then work out which has the lowest boiling point and which has the highest boiling point. *[However, the question is not a good one because the increasing number of O atoms (and thus the increasing number of electrons) would alone cause the boiling points of these substances to increase!]*

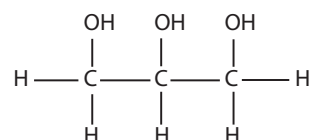
Propan-1-ol



Propan-1,2-diol
(Also known as Propylene glycol)



Propan-1,2,3-triol



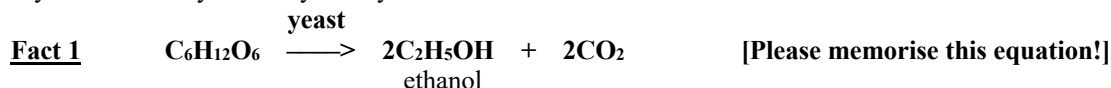
- The Syllabus requires you to know that the liquid that is put into the radiators of cars (*i.e. antifreeze*) is not water, but is in fact distilled water mixed with either ethylene glycol (ethan-1,2-diol) or is distilled water mixed with a combination of ethylene and propylene glycol (*i.e. both ethan- and propan-1,2-diol*) because these mixtures have a lower freezing point than water and a higher boiling point than water (which will help to prevent radiators from *boiling over* in hot countries). As it cools, water **expands between 4°C and 0°C**,⁷ and when it expands it does so with considerable force and this bursts the welded joints of a radiator – and the radiator then ceases to be watertight. In countries where the temperature drops below 4°C, **water should therefore NOT be used by itself (without antifreeze) in the radiators of cars/trucks/etc.**

⁶ If you need to revise the inter-molecular forces of attraction between molecules, then please do so.

⁷ Above 4°C water molecules flow easily around each other, but below 4°C the hydrogen bonds inside water **lock** all the molecules immovably into an **expanded** grid which occupies about 10% more space/more volume than liquid water does – therefore ice has a 10% greater volume than water.

B1 The anaerobic⁸ production of Alcohols from Sugars (i.e. by “Fermentation”)

- I know nothing about Biology – but I believe that the biological function of an enzyme is to act as a catalyst. Apparently “yeast” (which **is** a living organism) contains one or more enzymes (and enzymes are apparently **not** living organisms), and when a sugar is mixed with certain enzymes (e.g. the enzymes that are found in yeast), then “fermentation” takes place – *fermentation being the conversion of sugar into Alcohol in the presence of yeast*. For example, Glucose (C₆H₁₂O₆) can be fermented into Ethanol⁹ (C₂H₅OH) by using “zymase” the enzyme catalyst in “yeast”.



From glucose you will get ethanol (which is commonly called ‘Alcohol’ by people who drink ‘Alcohol’).

- When the Syllabus specifies the “*industrial production*” of Alcohol from **Sugar**, it is this reaction to which it is referring, and it is this reaction which you must quote in the exam. [In fact the syllabus should state that this is the “*industrial production of Alcohol for human consumption*”.¹⁰] Fermentation is an anaerobic process i.e. air is excluded from this reaction so that the Oxygen in the air does not oxidise the Alcohol into other products e.g. into Aldehydes.
- Fact 2** : You must also know that in sufficient concentration, Ethanol is poisonous/toxic to yeast, and if the concentration of Ethanol rises above 12% then the yeast starts to die, and by 15% all the yeast will have died. **When all the yeast has died, then the fermentation reaction will cease!**
- Therefore, it is not possible to make wines and beers with an Alcohol concentration higher than (I would guess something like) 14% – and in fact, although I have seen wine bottle labels that claimed an Alcohol content of 12-14%, I cannot remember ever seeing a label on a bottle that claimed an Alcohol concentration of more than 14%.
- You do not need to know more than these two facts about fermentation, but it is easily possible for the examiners to require you to use your brain and to put together two different parts of the course and ask you (for example) how spirits/fortified wines are made – and the answer is that since the catalytic converter of sugar into Alcohol (i.e. the yeast) is killed by the product of the reaction (when the Alcohol concentration reaches say 14-15%), then the only way to increase the Alcohol concentration of wine is to add Alcohol to the wine once it has been made. This process is called “**fortification**”. For example, “port” is a fortified wine viz. it has had Alcohol **added to it**.
- The Alcohol that is used to “fortify” wine can be obtained by using the method employed to obtain all “spirits” i.e. to distil fermented organic material to obtain the “Alcohol”. This is how all “spirits” (viz. gin/whisky/brandy/vodka/slivovitz/“pocheen”/etc) are made.
- The other thing that you ought to be aware of is that whilst Alcohol can be very enjoyable, it is *needed only by those human beings who are lacking in self-confidence*. *Even in fairly small dosages* Alcohol causes human beings to start to lose control over their actions (that is why you should never drink and drive); and, in larger amounts, a substantial loss of control can occur. Moreover, Alcohol can be addictive – and long term over-usage causes **severe** damage to the liver (i.e. cirrhosis of the liver), and excessive Alcohol consumption by a pregnant mother can harm an unborn baby. Additionally, there are some Alcohols (e.g. methanol) which even in small doses can cause blindness! ***Alcohols are actually HARMFUL substances for human beings, and you might like to make it a personal rule NEVER to drink more than say two units of Alcohol in any one day!*** *Alcohol can adversely affect your well-being (and your bank balance), and it may even ruin your health – and in excess it will most certainly ruin your life!*

⁸ “Anaerobic” reactions proceed without Oxygen. “Aerobic” processes require Oxygen.

⁹ Ethanol is often loosely referred to by the generic term “Alcohol”.

¹⁰ ... because (as we saw when we were talking about alkenes) the industrial production of Alcohol for *industrial* usage is carried out by the Hydration of the alkenes that are produced as a by-product of the cracking of long chained Carbon molecules to make petrol. Most people do NOT drink industrially produced Alcohol because it has no taste. It is only alcoholics who would drink it.

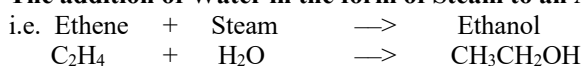
B2 The production of Alcohol from an Alkene

- If an Alcohol is going to be used for drinking purposes, then its flavour is very important (which is why it is produced by fermentation and then distillation – because this method imparts masses of different subtle flavours to the drink that is being consumed).
- However, if an Alcohol is NOT going to be consumed and is going to be used for industrial purposes (e.g. as a solvent for cleaning grease off fabricated metal parts), then its taste is unimportant/the taste is irrelevant – and the *most profitable method of production* will then be used.
- The most common way of producing Industrial Alcohol involves the Electrophilic Addition (the **Hydration**) of an Alkene by using (i) Phosphoric (V) Acid as the catalyst, or (ii) by using Sulphuric Acid as the catalyst.
- These reactions should be called the *Hydration* of Ethene into Ethanol. **“HYDRATION” is a reaction where Water reacts with a substance to form one new substance** e.g. $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$. *Actually, even though this is the official definition of “Hydration”, **any** hydroxy donation (e.g. by NaOH or KOH) can be called Hydration (but an “H⁺” species would still be needed to complete the reaction). After all, why should the “OH⁻” species come ONLY from water and not from [Na]⁺[OH]⁻ or from [K]⁺[OH]⁻?*

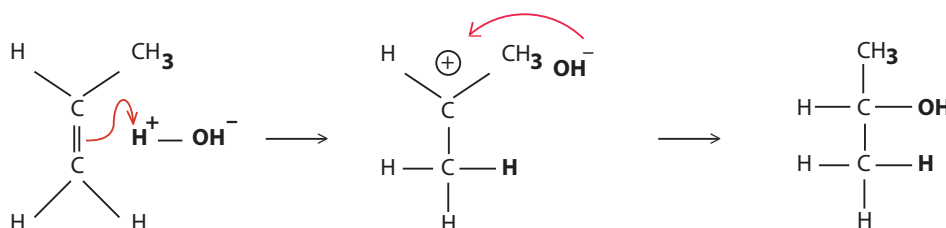
B2.1 The reaction of Ethene with Steam using H₃PO₄ as the catalyst

- An Alcohol can be produced by reacting an alkene with steam using an appropriate catalyst, and the reaction of an Alkene with Phosphoric (V) Acid as the catalyst is a classic one. **THIS is the one that you needed to know in your First Year** (in the Chapter on Alkenes), but let us look at it again.
- When water boils it becomes Steam, and since a molecule of Steam is essentially no different from a molecule of water where H⁺ and OH⁻ are in dynamic equilibrium with a molecule of H₂O [viz. $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$], then when Steam comes into contact with an *unsaturated* Carbon molecule, the electrophilic H⁺ species in the steam is attracted by the area of high electron density in the π bond of the unsaturated C molecule, and an Electrophilic Addition Reaction ensues with new C–H bonds and C–OH bonds being formed. [As the H⁺ species produced in “ $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ ” are used up, the reaction proceeds to the Right.]
- I will now draw (in its three stages) the Hydration reaction that occurs when Steam comes into contact with Ethene and you will see that the resulting product of the reaction is an Alcohol! NB You ARE required to know that the catalyst in this reaction is H₃PO₄, Phosphoric (V) Acid.

The addition of Water in the form of Steam to an Alkene (600K/60 atm/Catalyst H₃PO₄)



This is a straightforward Electrophilic Addition Reaction.



Markovnikov's rule tells us that the H⁺ ion will attach itself to the C atom that has more H atoms.

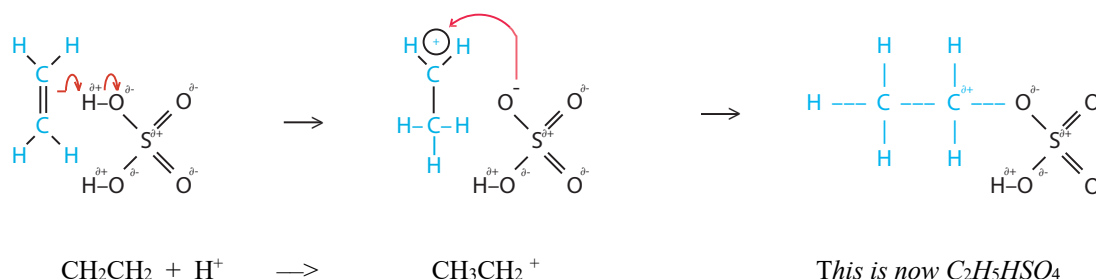
NB The H²⁺ part of an **un-ionised** water molecule could **in theory** collide with an alkene molecule and an electrophilic addition reaction might then take place – but the chances of such a collision taking place is **VERY small** because the two lone pairs of electrons on the O atom in the un-ionised water molecule would make the molecule nucleophilic and it would thus be repulsed by the area of high electron density in a π bond. The reaction that occurs therefore will almost certainly be the one above!

[The Hydration of an alkene can also be achieved using Sulphuric Acid, and the mechanics of the reaction are examined on the next page. The mechanics are not something that you will need at ‘A’ Level.]

NOT required knowledge for the 'A' Level Syllabus!

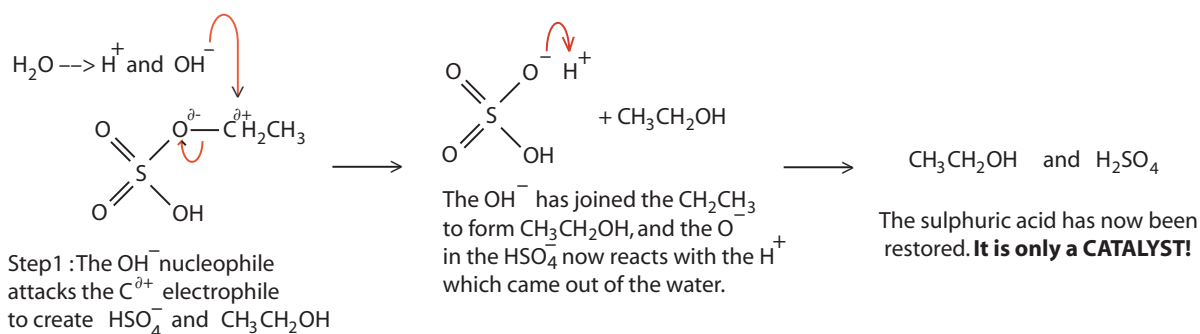
B2.2 The reaction of Ethene with Water using H_2SO_4 as the catalyst

Step 1 : Formation of Ethyl hydrogensulphate (add cold, concentrated H_2SO_4)



- An electrophilic addition reaction takes place between the ethene and one of the H^+ species on the sulphuric acid, and the first two stages above are thus the classic first two stages of an electrophilic addition reaction (the electrophile here being one of the two H^+ s on the sulphuric acid). The product formed is ethylhydrogensulphate – and this is merely an intermediary product/intermediary species that reacts with the water in the next stage below where the OH^- species from the water attacks the $\text{C}^{\delta+}$ in the ethylhydrogensulphate.

Step 2 : Formation of Ethanol (just add Water to the Ethyl hydrogensulphate)



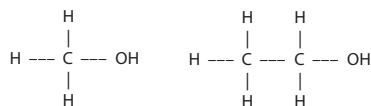
- The Syllabus does not require you to know the above, but I have included it for three reasons
 - because this is one of the ways in which industrial Alcohol is made (i.e. “industrial” in the sense that it is an Alcohol that is not for human consumption),
 - because dehydration is the reverse of Hydration and we will be studying dehydration in D4 of this Chapter, and most importantly, for the purpose of this Chapter, I have shown this reaction
 - so that I can illustrate how a catalyst works where *it is altered during the reaction, but where it is then fully restored by the end of the reaction*. You will remember that we said that “**A catalyst is a substance that alters the rate of a reaction without undergoing any permanent change to itself**”, and now you can see how a catalyst may be altered during a reaction, but *without undergoing any permanent change to itself*!

C Different sorts of Alcohols

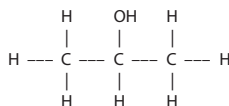
- Alcohols can be classified according to whether **THE C ATOM TO WHICH THE HYDROXY GROUP IS ATTACHED** is itself
 - attached to **no more than one** C atom – this being a **Primary (1°) Alcohol**
 - attached to **two** C atoms – this being a **Secondary (2°) Alcohol**
 - attached to **three** C atoms – this being a **Tertiary (3°) Alcohol**

- The following are the simplest examples of a

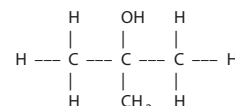
Primary (1°) Alcohol
(a) Methanol and (b) Ethanol
(BOTH of them are 1° Alcohols)



Secondary (2°) Alcohol
Propan-2-ol



Tertiary (3°) Alcohol
2-methyl-propan-2-ol



- Could you please note that this is NOT just an esoteric way of classifying Alcohols. In the same way that different Functional Groups have different reactions, so also Primary/Secondary/and Tertiary Alcohols all have different reactions (as we shall shortly see).

D The chemistry of Alcohols using Ethanol as the exemplar¹¹

D1 The combustion of Ethanol

- We have talked extensively about Combustion and I reproduce here the things that we discussed.

i) Combustion

- The verb “to combust” means “to burn”, and when something burns it reacts with Oxygen – therefore “combustion” is a form of “Oxidisation”.¹² *[NB Combustion is one form of Oxidisation – but there are other forms of Oxidisation! I hope that from “OILRIG” you will not have forgotten that “Oxidisation Involves the LOSS of electrons”.]*
- It is possible to extinguish the flame on a candle by putting a jam jar over the candle. What happens is that the jam jar stops the Oxygen in the air from reaching the flame, and the flame is thus extinguished. Clearly therefore,

COMBUSTION NEEDS OXYGEN

- Combustion occurs when something catches fire, and this can happen only in the presence of Oxygen. ***Oxidisation, however, does NOT need Oxygen. Combustion NEEDS Oxygen, but Oxidisation does NOT!*** *All that Oxidisation requires is a reaction in which electrons are LOST (the OIL bit of OILRIG), and there therefore has to be some other substance that will gain the electrons that are lost in this reaction.*

ii) The products of the Combustion of a Hydrocarbon

- When a Hydrocarbon combusts in an excess of Oxygen, then

NOTHING BUT Carbon Dioxide and Water are formed!

- However, if there is insufficient Oxygen present, then **Carbon MONOXIDE** and Water are formed (and some Carbon Dioxide may also be formed, but for ‘A’ Level purposes we assume that only Carbon Monoxide is formed).
- Now could YOU please write out the Reaction Equation for (a) the complete combustion, and (b) the incomplete combustion of Ethanol.

¹¹ An “exemplar” is a specific example of a phenomenon/a situation.

¹² The verb is “to oxidise” therefore the noun that is derived from that verb is “oxidisation” – and not “oxidation” as chemists carelessly write it! *Chemists sometimes use the English language in a wanton manner.*

D2 The conversion of Ethanol into Bromoethane

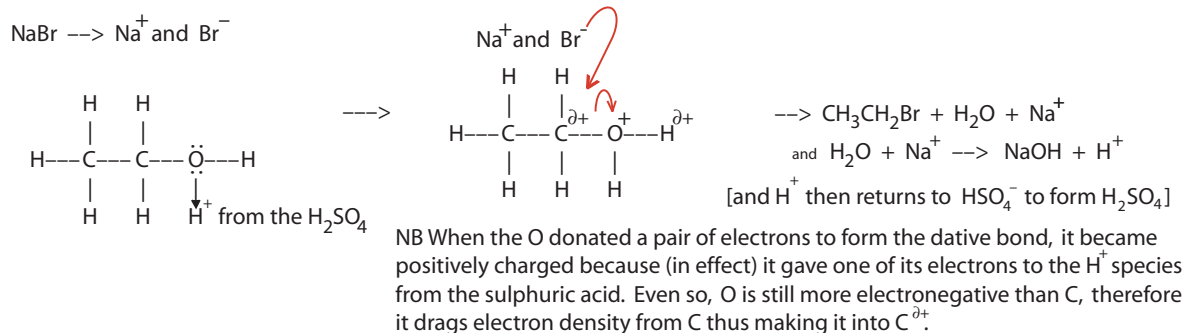
- This next bit is modestly complicated, and you do NOT need to know it. However I have included it here for those of you who have already started to develop a real interest in the “hows” and the “whys” of Chemistry so that you can see exactly how the reaction takes place, and because when I first studied this reaction for my ‘A’ Levels I could not understand **why the Br⁻ species choose to attack the C^{δ+} species rather than what at first sight looks like a MUCH more electrophilic O⁺ species**. If you also are curious about what happens, then do read on (otherwise please turn to the next page).

NB “Protonation” (cf. page 5) is an essential part of this reaction. Protonation occurs because the Sulphuric Acid, which by definition dissociates protons (*because that is what an acid does*), donates a proton to the Ethanol and **that is what starts off this reaction** – so remember, an acid is the catalyst of this reaction.

- In any/every Alcohol, the difference in electronegativity between the O atom and the C atom causes the C atom to become a C^{δ+} species.
- Left hand diagram below** : during the protonation, the O atom in the Alcohol donates a pair of electrons to the H⁺ species from the H₂SO₄ and a dative bond is created between the O atom and the H⁺ species. The O atom thus becomes an O⁺ species (as in the middle diagram) because it has now used TWO of its electrons to form the bond instead of just one electron – so in a sense *it has lost* one of its electrons to the H⁺ species (*whereupon H⁺ ceases to be a positively charged species*), and then the H species contributes that electron to form the bond between it and the O atom. However, the O⁺ species has used only one of the two unbonded pairs of electrons that it had, therefore it still possesses one unbonded pair of electrons. **The O⁺ species (despite the positive sign) has thus NOT become an electrophile, but it is still a NUCLEOPHILE!**
- The C^{δ+} species is so denuded of electron density by the electronegative O atom that it is highly susceptible to nucleophilic attack by the Br⁻ ion, and at the moment that the Br⁻ ion joins onto the CH₃CH₂ species, the C^{δ+}–O⁺ bond breaks heterolytically with the O⁺ species taking both the bonding electrons (to form a molecule of water) and thus the O⁺ species recovers its missing electron and ceases to be O⁺ after that. The C^{δ+} species on the Ethanol has meanwhile lost one of its electrons to what has become a molecule of water, therefore it has become a C⁺ species, and it and the Br⁻ species combine and form a C–Br bond.

This reaction is thus a NUCLEOPHILIC SUBSTITUTION reaction.

Formation of CH₃CH₂Br and H₂O (The species on the left is an ethanol molecule to which a proton has been donated by the sulphuric acid.) **Not** every step in the reaction has been shown below.

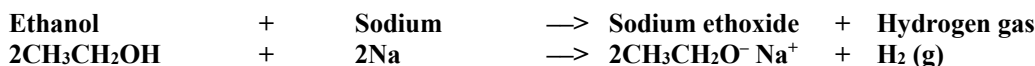


- OK, if you draw the dot-and-cross diagram for the middle step, you will see that although the O atom has “given” an electron to the H⁺ species and has thus become “O⁺”; nevertheless, “O⁺” here is NOT an electrophile because it still has one Lone Pair of electrons which makes it a **NUCLEOPHILE**. The Br⁻ nucleophile therefore cannot bond with it (**the Br⁻ nucleophile cannot bond with another nucleophile!**), and instead the Br⁻ nucleophile bonds with the C^{δ+} electrophile. **NOW do you see why the Br⁻ species attacked the C^{δ+} species and not the O⁺ species! Isn't Chemistry just so beautiful!**
- Actually, it is not the Chemistry that is beautiful. **It is the successful use of your brain to work out what is going on that is so beautiful.** I do hope that you are beginning to fall in love with your brain. Your brain is such a beautiful organ, and its successful stimulation will give you a great deal of pleasure all through your life!

- For the First Year Syllabus all that you need to know about the conversion of Ethanol into Bromoethane is that 1 this reaction occurs by “**REFLUXING Ethanol/NaBr/and H₂SO₄ until the nucleophilic substitution reaction is complete**”, and that
2 the reaction equation is “**CH₃CH₂OH + NaBr → CH₃CH₂Br + NaOH**”

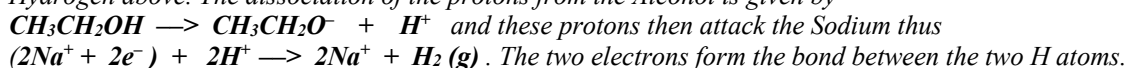
D3 The reaction of Ethanol with the metal Sodium (to form Sodium Ethoxide)

- An Alcohol dissociates a tiny amount of protons and thus (according to the Brønsted-Lowry definition) it behaves like a very weak acid; and, in the “How Far, How Fast Module” we will learn that some metals react with acids (at differing speeds) to form Hydrogen and the relevant Salt of the Metal – therefore the protons that an Alcohol dissociates will react with Sodium to form Hydrogen and the appropriate Salt e.g.



Please do not be put off by the fact that “CH₃CH₂O⁻ Na⁺” looks different from NaBr (Na⁺Br⁻) or NaCl (Na⁺Cl⁻). The fact is that each one of these three species is just an ionised “Salt”.

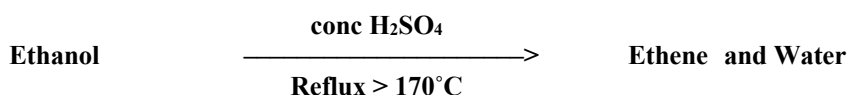
NB Metals consist of positively charged metal ions set in a sea of delocalised electrons, and it is the protons that Alcohols dissociate that react with the electrons in the sea of delocalised electrons of Sodium to form the Hydrogen above. The dissociation of the protons from the Alcohol is given by



D4 The “Dehydration” of an Alcohol (by Ejection/Elimination) to form an Alkene¹³

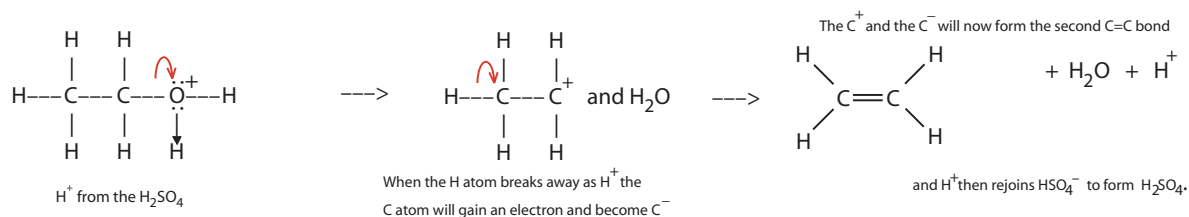
- You will remember that I showed you (on page 10) that when cold concentrated Sulphuric Acid and Ethene come into contact, then Ethyl Hydrogensulphate is formed, and then if Water is added, Ethanol will be formed – and that the reaction could be called the “Hydration” of Ethene to form Ethanol. Well, we have now come to the reverse of that reaction, and we can call it the “Dehydration” of Ethanol (because we are going to remove the hydroxy group that we attached to Ethene during its “Hydration”).
- For the First Year Syllabus, you **DO** need to know that
 - this reaction is called a “Dehydration” (by an Ejection/or an Elimination) reaction, and
 - that the reaction consists of
 - REFLUXING Ethanol
 - with an **EXCESS of concentrated H₂SO₄** (more H₂SO₄ than Ethanol)
 - at not less than 170°C¹⁴**

Just as the bromination of an Alcohol starts with a protonation reaction, so also the dehydration of an Alcohol is started off by the protonation of the Alcohol by the Sulphuric Acid. Refluxing for a long period of time is necessary to break the “C–O” and the “C–H” bonds (as in the diagram overleaf) to create the Ethene.



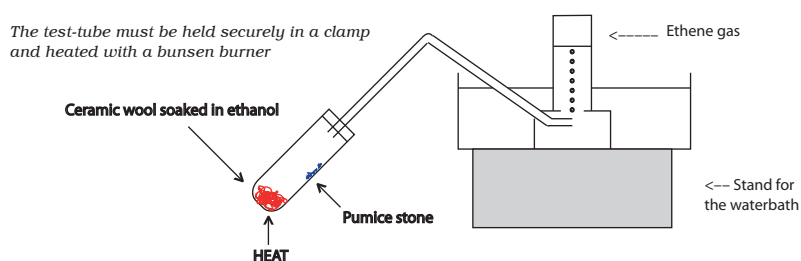
¹³ One of the other official names for this reaction is an “Elimination” reaction. However, since water is ejected or is spat out in this reaction, “Elimination” is an otiose name – and this reaction should today really be called an “Ejection” reaction. To “eliminate” in English today means something totally different from what it did 100 or whatever years ago. One product from an “elimination/ejection” reaction, will be an unsaturated molecule.

¹⁴ If you do it with an excess of Ethanol **at 140° C**, then an Ether will be formed.



Here, the sulphuric acid is a catalyst.

- The process is an *industrial* (i.e. large scale) process, but exactly the same reaction can be demonstrated in the laboratory by soaking a piece of **ceramic** wool in Ethanol/dropping the ceramic wool to the bottom of a test-tube/tilting the test-tube sideways and then sliding a piece of pumice stone (which is Aluminium Oxide, Al_2O_3) down the side of the test-tube/putting a bung with a hollow tube into the top of the test-tube/and then heating **the pumice stone**/ Al_2O_3 over a flame. The vapourised Ethanol will be dehydrated by the pumice stone catalyst and it will then form Ethene (and this can then be collected over water).



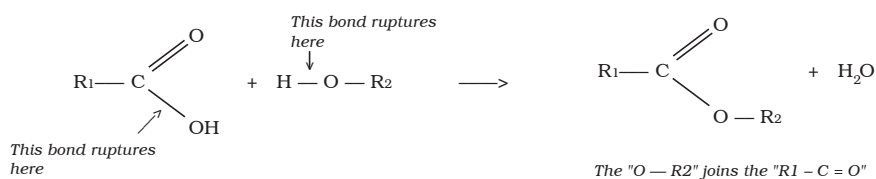
COTTON wool must not be used because it would catch fire.

- If the liquid in the water bath had been Br_2 (aq), then it would have been decolourised immediately – **even in the dark**, and even if the Br_2 (aq) had been freezing cold. *If you do not understand what I have just said, then you have forgotten the classic test to see whether a substance is an alkane or an alkene! You must remember this test for your exam!*

D5 Reacting an Alcohol with a Carboxylic Acid to form an Ester

- For the Esterification of an Alcohol, the Syllabus requires you to know that
 - “an **Alcohol** and a **Carboxylic Acid** must be **REFLUXED** in the presence of concentrated H_2SO_4 until Esterification takes place”, and then
 - you must draw the diagram (for example) of Ethanol and Butanoic Acid (cf. below).

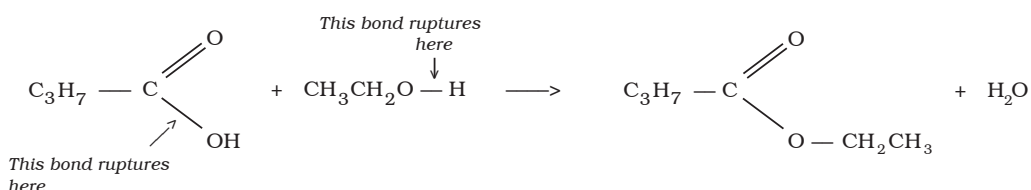
- Generically, $\text{R}_1\text{COOH} + \text{R}_2\text{OH} \xrightarrow[\text{Reflux}]{\text{conc. H}_2\text{SO}_4} \text{R}_1\text{COOR}_2 + \text{H}_2\text{O}$
- Please note that R_2COOR_1 is not formed! R_2COOR_1 and R_1COOR_2 are NOT the same Ester** (page 16 of Chapter 1 of First Year Organic chemistry will remind you of this), **and R_2COOR_1 IS NOT FORMED**, therefore please note carefully in the diagram overleaf the exact place at which each one of the two bonds breaks.



A double bond is stronger than a single bond, therefore the single bond in the acid is the one that ruptures.

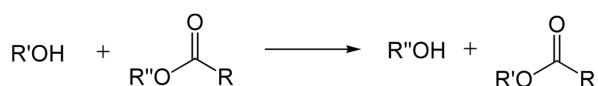
NB In Organic Chemistry, it is **not** important to show the non-organic products of a reaction therefore it is **NOT necessary** to show the water formed in this reaction. However I like to show it because then I can check that my equations are stoichiometrically correct (i.e. the moles in the equation are in the right proportions).

- When the reaction is completed, the resulting solution can be distilled and the Ester thus separated from the unreacted reactants/catalyst.
- Thus, Butanoic Acid + Ethanol \longrightarrow Ethyl butanoate¹⁵ [$\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$] + Water



- Please note that a Carboxylic Acid will react with an Alcohol in the presence of a strong acid to form an Ester, and also an Ester can be hydrolysed in the presence of a strong acid into a Carboxylic Acid and an Alcohol. **The reaction is thus a reversible one.** It is better therefore to hydrolyse an Ester into a Carboxylic Acid in the presence of a strong base (rather than a strong acid) because that is not a reversible reaction.

NB It is possible to swap one part of an Ester with a similar species from another Alcohol



Source: Wikipedia

and this reaction is known as “**Tranesterification**”.

E THE OXIDISATION OF ALCOHOLS : “OILRIG”

- I hope that you will not have forgotten that “Oxidisation Involves the LOSS of electrons”.*

Abnormal/Aggressive Reaction Conditions

- The **AGGRESSIVE** Oxidisation of ANY Alcohol that results in the rupture of Carbon to Carbon bonds inside the Alcohol could cause differing **Carboxylic Acids** to form, therefore in all that follows below, I shall be talking solely about the **GENTLE** Oxidisation of Alcohols where the Oxidising agent is usually a Dichromate ion.

NORMAL Reaction Conditions

- Primary and Secondary Alcohols become converted into differing substances under **GENTLE** Oxidisation. The normal Oxidising agent used in a laboratory is either Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) or Sodium Dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), and $\text{Cr}_2\text{O}_7^{2-}$ [the Chromate (VI) ion] is called the Dichromate ion.¹⁶

NB Potassium dichromate (Cr^{6+}) rapidly converts into the Cr^{5+} form – and this is a HIGHLY carcinogenic substance. Please do be careful with it (and dispose of it appropriately).

¹⁵ Remember to ask yourself what the “-oate” molecule is (here it is a butanoate), and then ask what sort of butanoate it is (here it is an ethyl butanoate).

¹⁶ You may think that Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) should really be called “**Dipotassium dichromate**”; but, although I would agree with you, one thing that you must learn early in your life is which battles to fight and which not to fight – and there is no point fighting this one, so let us just accept the name by which it is universally known i.e. Potassium Dichromate.

- Potassium dichromate is bright orange-red colour in its solid form (cf. page 31), and if you were to calculate the Oxidisation state of Chromium in $K_2Cr_2O_7$ then you would find that it is Cr^{6+} , and if you did the same for Manganese in $KMnO_4$ you would see that it was Mn^{7+} . “7+” *implies* that the Manganese ion has had one more electron removed from it than Chromium in Cr^{6+} – and this in turn implies that Manganese is more ‘desirous’ of recovering electrons than is Chromium viz. **Mn^{7+} is a stronger oxidising agent than Cr^{6+} .** However, please remember that these are merely oxidation numbers. **Chromium has not actually lost 6 electrons, nor has Manganese actually lost 7 electrons.**
- The MnO_4^- (Manganate) ion in Potassium Permanganate (i.e. $KMnO_4$) is an oxidising agent, but it is a *more* aggressive oxidising agent than the Dichromate ion. For the oxidation of an Alcohol, the Dichromate ion is more suitable than the Manganate ion. The MnO_4^- (Manganate) ion will oxidise a Primary Alcohol completely into a Carboxylic Acid. The reaction might not stop at the Aldehyde stage – therefore we do NOT use MnO_4^- as the oxidising agent in this reaction.

The differing OXIDISATION reactions of 1°, 2°, and 3° Alcohols

- If you are wide awake at this point, you will remember that there are different sorts of Oxidisation reactions (of which “Combustion” is one of them). Here, I am going to tell you about another sort of Oxidisation reaction. Could you please note carefully, that in this reaction the Oxygen that is being provided for the Oxidisation is written “ [O] ” i.e. **the Oxygen atom is written inside a square bracket!**
- I told you earlier that Primary (1°), Secondary (2°), and Tertiary (3°) Alcohols can behave very differently from each other, and now I am going to show you some examples of this happening – and in all three of the following Oxidisation reactions, I am going to use Sulphuric plus and an excess of a Chromate (VI) ion¹⁷, i.e. a Cr^{6+} ion (from say either Potassium or Sodium Dichromate) to provide the **Oxidising agent**. *Both the Chromium and the Potassium ions will become Sulphates during these reactions (cf. the Appendix).*
- The first of these three Oxidisation reactions is the conversion of a Primary (1°) Alcohol into an Aldehyde – and if you mix a 1° Alcohol with concentrated Sulphuric Acid¹⁸ and an Oxidising agent such as Potassium Dichromate in a test tube, **then just the heat from your hand will cause the 1° Alcohol to be Oxidised into an Aldehyde**, *but if you subsequently heat the mixture then you will cause the Aldehyde to be further Oxidised into a Carboxylic Acid.*

PLEASE COULD YOU NOW LEARN THESE THREE REACTIONS OFF BY HEART!

Under **GENTLE** Oxidisation, (I will repeat that, under **GENTLE** Oxidisation)

Primary (i.e. 1°) Alcohols → **ALDEHYDES**, and then **ALDEHYDES** → **CARBOXYLIC ACIDS**.
Secondary (i.e. 2°) Alcohols → **KETONES**.
Tertiary (i.e. 3°) Alcohols : **RESIST GENTLE OXIDISATION**.

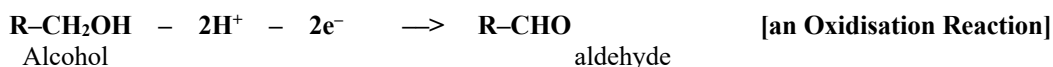
- This is one of the classic tests for the oxidation of an Alcohol into either an aldehyde or into an acid, so learn it off by heart “Orange to Green, **ORANGE TO GREEN, ORANGE TO GREEN!** Please never forget that: **ORANGE** to **GREEN**”! The Chromate (VI) ion has an orange colour – but the Cr^{6+} ion will be *reduced* to a blue Cr^{3+} ion during the reaction – therefore as the blue Cr^{3+} ion is formed it mixes with the orange Cr^{6+} ion, and in Physics (and in painting) when orange and blue are mixed together the resulting colour appears to be green.
- I have not asked you to do any Oxidisation Number calculations since the Foundation Module, so could you now please calculate the Oxidisation Numbers of **Cr** in $K_2Cr_2O_7$, and in $Cr_2(SO_4)_3$. [The answers that you should have arrived at are “+6” for **Cr** in $K_2Cr_2O_7$ (and Cr^{6+} has an **orange** colour) and “+3” in $Cr_2(SO_4)_3$ (and Cr^{3+} has a **blue** colour¹⁹). *[I trust that you remember that you have to reverse the sign and the number when they are shown as an exponent integer i.e. the number “+3” becomes the oxidation state Cr^{3+} , but Americans tend not to do so.]*

¹⁷ The orange $Cr(VI)$ ion is the Oxidising agent, and you will need *AN EXCESS* of it – otherwise you will run out of the Oxidising agent before the reaction is completed!

¹⁸ It will not work with **dilute** H_2SO_4 .

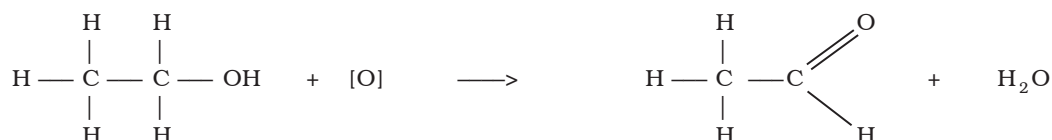
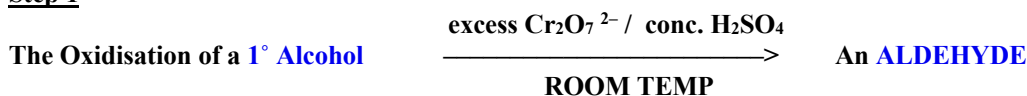
¹⁹ Some people say it is blue, others say it is green. **Please do not get hung up on the colour.**

NB In Organic Chemistry it is permitted to use an Oxygen atom inside square brackets, i.e. “[O]”, to indicate that Oxygen is oxidising an organic substance. You will see this convention used on the next few pages. In modern Chemistry notation, we also tend NOT to show the electrons that are being lost by the Alcohol in the reaction. For example we no longer write



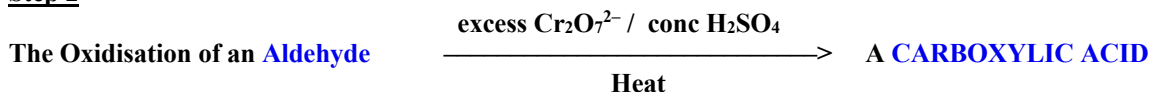
E1 The Oxidisation of Primary Alcohols (1° Alcohols) into first Aldehydes and then into Acids (The mechanisms of these reactions is not shown and it is not required.)

Step 1



NB You must have an excess of $\text{Cr}_2\text{O}_7^{2-}$ otherwise you will run out of the Oxidising agent before the reaction is completed! You do not need to show the Water if you do not want to do so.

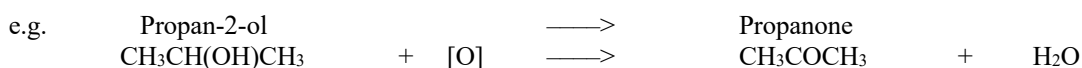
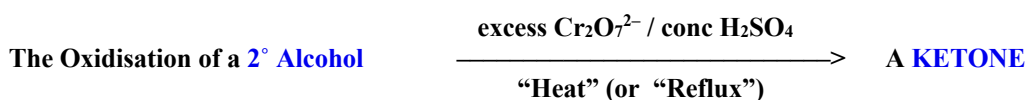
Step 2

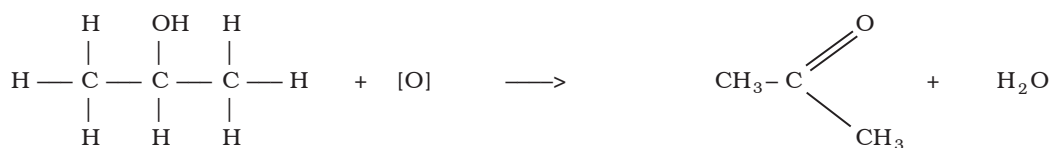


NB You must have an excess of $\text{Cr}_2\text{O}_7^{2-}$ otherwise you will run out of the Oxidising agent before the reaction is completed!

The overall reaction from an Alcohol to an Acid is thus $\text{CH}_3\text{CH}_2\text{OH} + 2[\text{O}] \longrightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$.

E2 The Oxidisation of Secondary Alcohols (2° Alcohols) into Ketones





NB You must have an excess of $\text{Cr}_2\text{O}_7^{2-}$ otherwise you will run out of the Oxidising agent before the reaction is completed! You do not need to show the Water if you do not want to.

E3 The Oxidisation of 3° Alcohols

- **3° Alcohols “RESIST GENTLE OXIDISATION” !**

This is the precise phrase that you must use! In other words, as long as you do not use abnormal/aggressive Oxidising conditions, then a Tertiary Alcohol will not turn into an Acid.

NB You may remember that I said that if you REFLUXED a 3° Alcohol aggressively you would rupture the Carbon to Carbon bonds, and differing Carboxylic Acids could form. Well, this is where that would happen. 3° Alcohols **resist GENTLE oxidation**, but if you inject too much energy into the reaction, then you would burst the C-C bonds, and Carboxylic Acids could form. Therefore, do remember that [here we have been talking about the GENTLE Oxidisation of Alcohols](#).

- The Oxidisation of Primary/Secondary/and Tertiary Alcohols are **frequently** tested in your exams, so let me repeat what I have already told you!
- [Reactions of/Tests for 1° vs. 2° vs. 3° Alcohols](#)

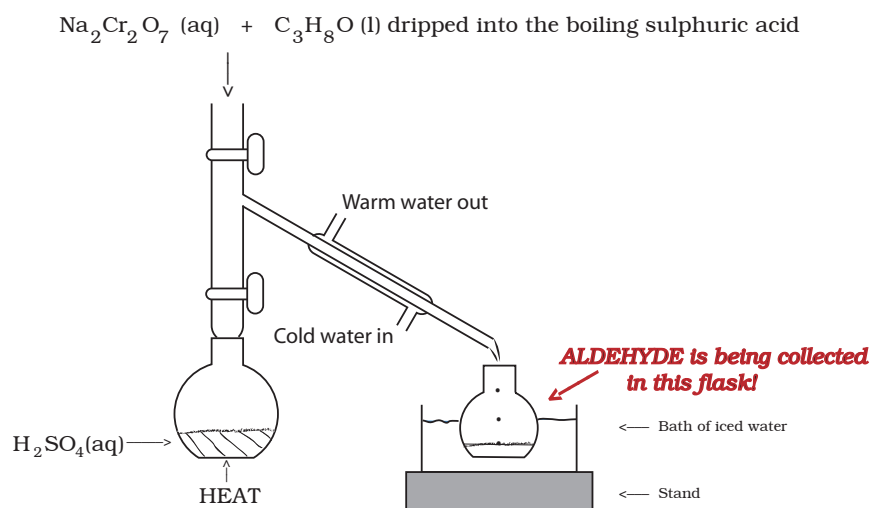
Under GENTLE Oxidisation, (I will repeat that, under GENTLE Oxidisation)

1° Alcohols → ALDEHYDES, and then ALDEHYDES → CARBOXYLIC ACIDS.
 2° Alcohols → KETONES.
 3° Alcohols : resist gentle oxidation.

- In some textbooks and in some exam questions, the instruction “*Reflux*” is used when talking about the Oxidisation of an Alcohol, and this is a correct but misleading instruction because the instruction “reflux” implies that you need to heat the reactants for a long time in order for the reaction to take place.
- When converting a 1° Alcohol into an Aldehyde, care must be taken not to then convert the resulting Aldehyde into a Carboxylic Acid.
- You may also see a distillation diagram for the production of an Aldehyde, and in the diagram it could say “Heat” – and you will immediately say to yourself “OK, if the Alcohol is a 1° Alcohol, then in the presence of concentrated H_2SO_4 and an Oxidising agent it is being Oxidised into an Aldehyde, and because the Aldehyde is being **heated** then it is IMMEDIATELY being converted into a Carboxylic Acid”.
- What is actually happening in the set-up on age 19 is that (because Aldehydes are not Hydrogen bonded they have a much lower boiling point than either an Alcohol or a Carboxylic Acid therefore)²⁰ **the Aldehyde is being distilled off as soon as it forms**. As it happens, the Oxidisation of an Aldehyde into a Carboxylic Acid takes place with so little heat that some of the Aldehyde in this apparatus IS INEVITABLY being converted into a Carboxylic Acid – *but Carboxylic Acids have a much higher boiling point than Aldehydes (see footnote 20) therefore the acid is being LEFT BEHIND in the distillation flask*.
- However, if you encounter a similar diagram in your exam, I hope that now that I have warned you of the pitfall, you will not fall into the trap of thinking that an Aldehyde cannot be what is being formed in this experiment/exam question.

²⁰ For example, the boiling points (in °C) of Ethanal/Ethanol/and Ethanoic Acid are 20.8/78.5/and 118 respectively.

- *Students sitting exams are already under a lot of pressure, and to set them “trick” (or even worse ‘stupid’) questions is WRONG because it panics them and they are then not able to demonstrate the knowledge that they actually DO possess.*
- An alternative to the set-up below would be to drip the oxidising agent, $\text{Na}_2\text{Cr}_2\text{O}_7$, into the warm H_2SO_4 and Alcohol but I don’t like heating Alcohol – it is very volatile. In any case, AS Level students learn that reacting an Alcohol with conc. Sulphuric Acid can produce either an Ether at 140°C (or an Alkene at 170°C) so what is the point of confusing them by heating the acid and the Alcohol together. I prefer the set-up below. **NB You could warm a test-tube (with all the reactants in it) in your hand and the reaction would take place! Heating increases the risk of the corresponding acid being formed.**



- The reaction equation that was given in the exam paper of May 2002 was $3\text{C}_3\text{H}_8\text{O} + \text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 \rightarrow 3\text{C}_3\text{H}_6\text{O} + \text{Na}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}$ and it is *wrong* in the sense that it conveys the **false impression** that ALL the Product ($\text{C}_3\text{H}_6\text{O}$) is either an Aldehyde or a Ketone, and that none of it is a Carboxylic Acid (because a Carboxylic Acid would have TWO Oxygen atoms in its molecular formula, and the Product here clearly has only ONE Oxygen atom in its molecular formula!). In my opinion, this was really an **EXTREMELY BAD** question for the examiners to have set in an exam.

Test to distinguish an Aldehyde from a Ketone

- On earlier pages we saw that when in the presence of an excess of an acidified dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) provided by for example $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 (*dilute sulphuric acid will not allow the reaction to occur*), the ($\text{Cr}_2\text{O}_7^{2-}$) acts as an oxidising agent and provides the Alcohol with oxygen (which is written as “[O]” and the Alcohol is then converted as follows

Primary Alcohols → ALDEHYDES, and then ALDEHYDES → CARBOXYLIC ACIDS.
Secondary Alcohols → KETONES, and
Tertiary Alcohols : resist gentle oxidation.

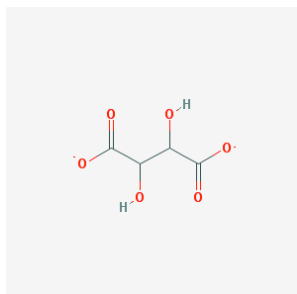
and that while the dichromate ion is providing oxygen for the oxidation to take place, the orange Cr^{6+} ion is reduced to a blue Cr^{3+} ion (and the orange/yellow and the blue coloured substances together look green). **The colour change of orange to green thus indicates where the oxidation reaction is taking place – and if there is no colour change, then no oxidation is taking place.**

- Let us say that we had three test tubes and in each one there was just one of three Alcohols viz. a 1° , a 2° , and a 3° Alcohol, and there was a fourth test-tube with the excess Potassium dichromate and conc. sulphuric acid in it – and all four test-tubes were in a bath of hot water (and this would get all the liquids to the same temperature).

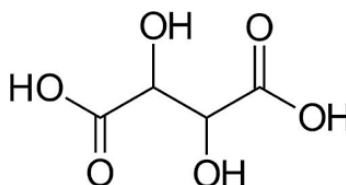
- If I were then to put an equal amount of the acidified dichromate into each of the test-tubes with the Alcohols, then two of the test-tubes would go from orange to green because
 - The 1° Alcohol was being turned into an Aldehyde (or into a Carboxylic Acid).
 - The 2° Alcohol was being turned into a Ketone, and
 - there would be no colour change in the third because 3° Alcohols are not oxidised under these conditions.
- A lack of a colour change would thus identify the test-tube which had the 3° Alcohol in it – *but how would we know which test-tube contained the 2° Alcohol and which the 1° Alcohol?*

Aldehyde or Ketone

- Luckily there is another simple colour change test that we can utilise to identify an aldehyde from a ketone (and thereby identify the 1° Alcohol from the 2° Alcohol). There are three substances that will help us to distinguish Aldehydes from Ketones. They are colourless Tollen's reagent/Fehling's **solution** and Benedict's **solution**. The latter two solutions are coloured blue by the dissolved copper sulphate Cu^{2+} (aq) ions in them.²¹
- All three substances are oxidising agents and will oxidise the Aldehyde into a Carboxylic Acid **but will not oxidise the Ketone into anything** – and (by definition) the oxidising agents themselves will thus be reduced from soluble Cu^{2+} sulphate ions to (in this case) insoluble Cu^+ oxide ions, and thus the Cu^+ ions precipitate out to give a dirty reddy/brown solution initially (but given enough time the copper oxide particles will settle to the bottom of the test-tube to leave a colourless solution).
- Having identified the 3° Alcohol by the lack of a colour change from orange to green, we can then identify the 1° Alcohol by the colour change from blue to dirty reddy/brown, and the 2° Alcohol will be in the test-tube where the blue coloured solution has not altered.
- If (when talking about Fehling's solution) the textbook that you use in your school talks about 2,3-dihydroxybutanedioate ions (also known as potassium sodium tartrate or Rochelle salt), then this is what such a species looks like.



and it comes from 2,3-dihydroxybutanedioic acid, and it contains one acid functional group ($-\text{COOH}$) at each end of the molecule (and two Alcohol functional groups in the middle of the molecule).



Source: https://en.wikipedia.org/wiki/Tartaric_acid

but if your textbook does talk about the above, then **just glance at it and move on**.

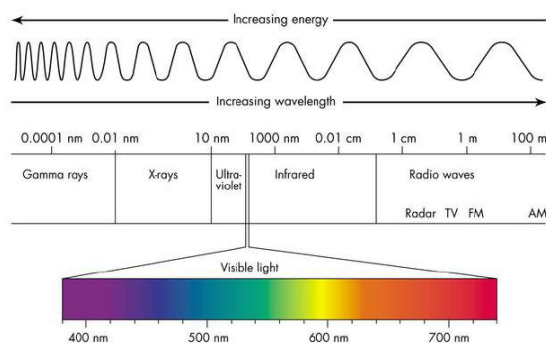
- **That for the moment is more than enough about 1° / 2° / and 3° Alcohols.**

²¹ Both solutions involve “complexes” and “ligands” and we will talk about complexes and ligands elsewhere. You need $(\text{OH})^-$ ions in both the Fehling's and Benedict's complex, and we will talk about how this is achieved.

F Identification of differing Carbon compounds using Infra-red Spectroscopy

*NB It is only those organic molecules that have a **dipole moment** that is capable of being altered that absorb IR radiation. The absorbed IR radiation causes them to **stretch** (symmetrically or asymmetrically) along their bond lengths, or else their bond angles fluctuate i.e. they “**bend**”!*

- I hope that you know enough GCSE Physics to know that “white” light contains the seven basic colours of the spectrum (viz. Red/Orange/Yellow/Green/Blue/Indigo/and Violet) – and that each of these colours is the perception that registers in the brain when a particular band of electro-magnetic radiation enters the eye, and that there are many other forms of electro-magnetic radiation (or electro-magnetic waves) that are not visible to the human eye e.g. infra-red waves/X-rays/radio-waves/etc.
- For example, when you go to have a broken limb X-rayed in a hospital, the machine is sending a brief pulse of a particular waveband of electro-magnetic radiation (viz. X-rays) through your body. Equally, the burglar alarm detectors that you have in your house pick up the infra-red waveband emissions that human beings emit. “Infra-red” is a bastardised English and Latin combination of words to mean “below the red” waveband; and, “ultra-violet” is another combination of Latin and English words to mean “beyond” or in this case “on the other side of the violet” waveband.



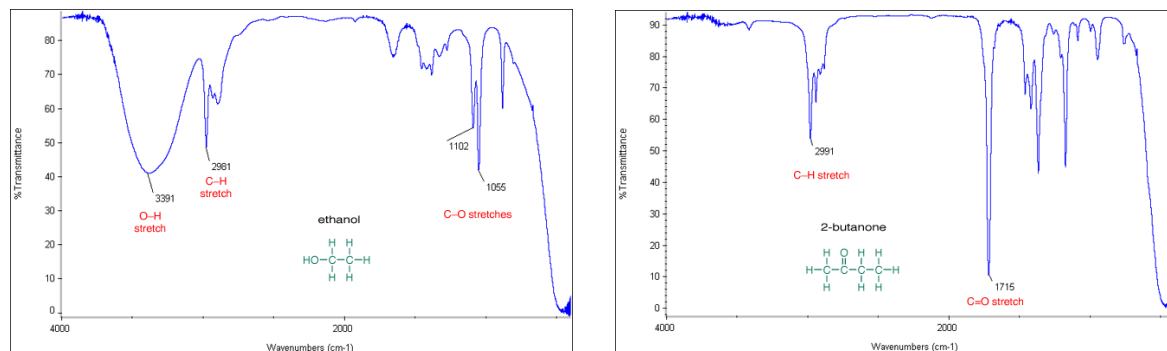
Source : <http://www.antonine-education.co.uk/index.htm>

- For the analysis of Alcohols we use machines that direct pulses of infra-red (IR) radiation²² at the substance that is being analysed, and then the radiation that passes through (i.e. the radiation that is “transmitted” and thus not absorbed by²³) the substance is recorded and analysed. However, as the infra-red radiation passes through the substance, different Functional Groups in the substance will absorb differing amounts of infra-red radiation at differing wavelengths – and since Chemists know which Functional Groups absorb exactly which bits of the infra-red waveband, then (merely by analysing the bits of the infra-red waveband that the molecule has absorbed) it is relatively easy to say which Functional Groups are present in any particular Carbon compound.
- In reality, the analysis of IR spectrographs is extraordinarily skilled work – but, luckily, all that you need to know is how to recognise the presence of the following Functional Groups in a Carbon compound
 - an **Hydroxy Group** viz. one that has an “O–H” group bonded to a C atom
 - a **Carbonyl** compound viz. one that has a “C=O” bond in it, and
 - a **Carboxylic Acid** viz. one that contains BOTH of the Functional Groups above on the same C atom.
- The IR spectrographs that you will be given to analyse will have Wavenumber (i.e. the inverse of Wavelength) as the X-axis, and the amount of the IR radiation that has gone through the substance (i.e. the “Transmittance”) as the Y-axis. The y-axis starts at “zero” Transmittance (i.e. 100% Absorbance) and gets larger as it goes upwards, therefore **the more IR radiation that the substance has absorbed, the bigger will be the downward spike on the graph.**

²² of wavelength 2.5×10^{-4} right up to 1.5×10^{-3} .

²³ “Transmittance “ of 100% = Absorption of 0%, and vice versa.

- However, one thing that you **must** be aware of is that different Functional Groups have different spectrographs when they are in different molecular combinations. For example, the “O–H” group has one definitive spectrograph in an Alcohol, but it will have a different one in a Carboxylic Acid! You just have to learn to recognise the different spectrographs e.g. below is the IR spectrograph of Ethanol and Butanone, but do not worry about it because you will NOT be tested on IR spectrographs in any great detail in your exams.



Source : University of Colorado.

- In the exam you will be given a data sheet headed “Spectroscopy”, and on it you will see that

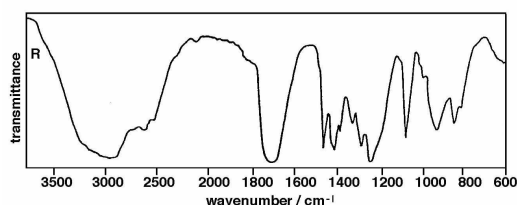
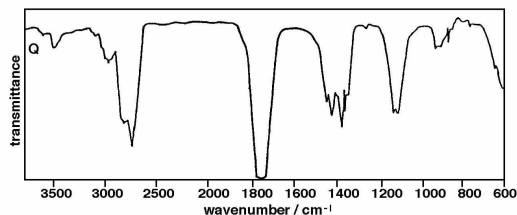
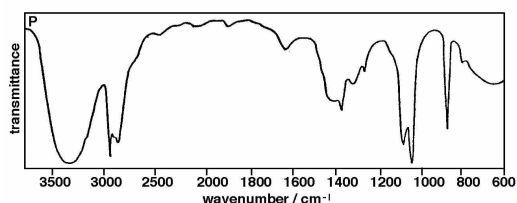
	Wavenumber cm^{-1} (inverse of wavelength)
• C–O bonds in <u>Alcohols/Ethers/Esters</u>	have a characteristic absorption at 1000–1300
• C=O bonds in <u>Aldehydes/Ketones/Acids</u>	have a characteristic absorption at 1680–1750
• O–H bonds in <u>Acids</u>	have a characteristic absorption at 2500–3000
• O–H bonds in <u>Alcohols/Phenols</u>	have a characteristic absorption at 3250–3550

- I have taken the infra-red spectrographs on the next page straight out of a past exam paper, so that in the exam you will recognise which spectrograph indicates which Functional Group. Please note that (i) because the Wavenumber is the inverse of the Wavelength, the numbers on the x-axis **diminish** as you go from left to right, and that (ii) because Transmittance is the complement of Absorbance, it is the **downward spikes** at characteristic values that identify the different Functional Groups!
- The examiners could easily and justifiably combine different parts of the Syllabus, and give you the Spectrographs of Ethanol/Ethanal/and Ethanoic Acid, and I have therefore deliberately chosen these spectrographs to show you on the next page.
- Please memorise the differences in these three graphs** – and then when you meet them in the exam you will recognise them and you will unhesitatingly identify them. The examiners will not always ask you to recognise Ethanol/Ethanal/and Ethanoic Acid, and could easily give you Propanol/Propanal/and Propanoic Acid – but the principles involved will be the same.
- They did not do so when I was a young man, but today when girls go out clubbing and are dressed up ready to go out, they apparently say to each other “*Does my bum look big in this dress?*”. Well, if that is a phrase with which you are familiar, then you have a super way of remembering the difference between the shape of the spike of an O–H bond in Alcohols and phenols and the shape of the spike of an O–H bond in Carboxylic Acids, because an O–H bond in Carboxylic Acids has a “big bottom” whereas the spike of an O–H bond in Alcohols and Phenols is (by comparison) quite a “small bottom”!²⁴
- The graphs overleaf are taken from a past OCR exam paper (and examinees were required to be able to recognise Ethanol/Ethanal/and Ethanoic Acid from the graphs).

²⁴ Please do not talk about bums/bottoms in your exam. There are no marks allocated in the Marking Scheme for such references. I have done so merely to make the explanations involved more vivid/more memorable.

- 1) The first graph has a small bottom between 3,000 and 3,500 therefore it is not an acid. Compare this bottom to the size of the bottom in the third graph (which is an acid) and you will see the difference. If the first graph is not that of an acid, then (from the choices given in the question) it has to be either an Alcohol or an Aldehyde.
 - 2) There is a C single bond O (“C–O”) spike at about 1,050 and, since an Aldehyde does not have a “C–O” bond but has a “C=O” bond and a “C–H” bond, then the first graph must be that of an Alcohol.
 - 3) The second graph has a “C=O” spike at about 1,750 and it has no “O–H” spike at around 3,000 to 3,500 therefore the graph must be that of the Aldehyde.
 - 4) The third graph has the big bottom “O–H” spike of an acid and it also has the “C=O” spike at 1,750 therefore it must be that of the acid.
- It does not matter what the textbooks might tell you (nor indeed how easy it looks on CSI Miami or whatever), the reality is that the interpretation of IR graphs is **VERY** complicated and it takes a long time to master the interpretation of these graphs – therefore it is impossible for the examiners to set you a *difficult* question to answer regarding such graphs. At this stage of your understanding of Chemistry you are not a forensic scientist, therefore the examiners can set you nothing but *easy* questions to answer! Therefore, don’t worry about these graphs. Learn what you need to know and then use your brains in the exams and you will score the maximum marks!

(d) The following three infra-red spectra were obtained at different stages of an oxidation reaction of an organic compound.



Identify the important absorptions present in each of the spectra, P, Q, and R, and hence the functional groups present at each stage of the oxidation.

[7]
[Total:25]

This one is the Alcohol

“C–O” spike at 1,050 and whilst it does have an “O–H” spike, it has no big bottom “O–H” spike at around 3,000.

This is the Aldehyde

A “C=O” spike at 1,750 and no “O–H” spike at all. (Aldehydes have a “C–H” but no “C–OH” bond.)

This is the Acid

A “C=O” spike at 1,750 and a big bottom “O–H” spike at around 3,000.

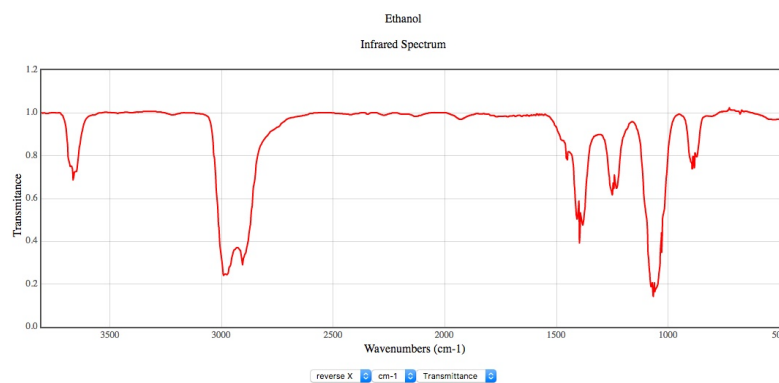
NB If you cannot recognise the molecular structure of different substances (i.e. which have double bonds/etc), then you would not be able to answer this question.

- You must be able to recognise the characteristic spikes²⁵ for
 - an O–H bond that is not a part of an acid (i.e. not part of a COOH group)
 - an O–H bond that **is** part of an acid
 - a C–O bond, and
 - a C=O bond.

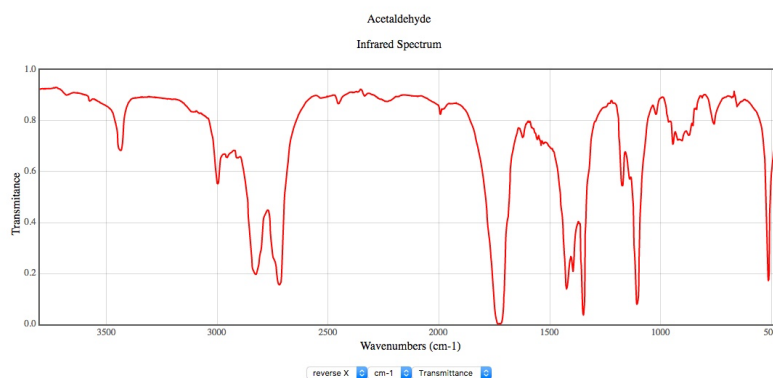
²⁵ A “spike” is the inverse of a peak.

- **If required to do so**, your answer should state something like this : “For the given Carbon compound, the spectrograph contained the characteristic spikes
 - of an O-H bond in a COOH group at $2500\text{--}3000\text{ cm}^{-1}$, and
 - of a C–O bond at $1000\text{--}1300\text{ cm}^{-1}$, and
 - of a C=O bond at $1680\text{--}1750\text{ cm}^{-1}$,
 therefore the substance must have been a Carboxylic acid.
[Obviously if the spectrograph had been that of an Alcohol or an Aldehyde, then your answer would have been worded differently. NB The characteristic absorption wavenumbers will be given to you in the data booklet provided in the exam.]
- If you are interested, you can find an enormous amount of data about different substances at the US National Institute of Standards and Technology
<http://webbook.nist.gov/cgi/cbook.cgi?ID=C64197&Type=IR-SPEC&Index=2>
 and I have taken the next three graphs from there

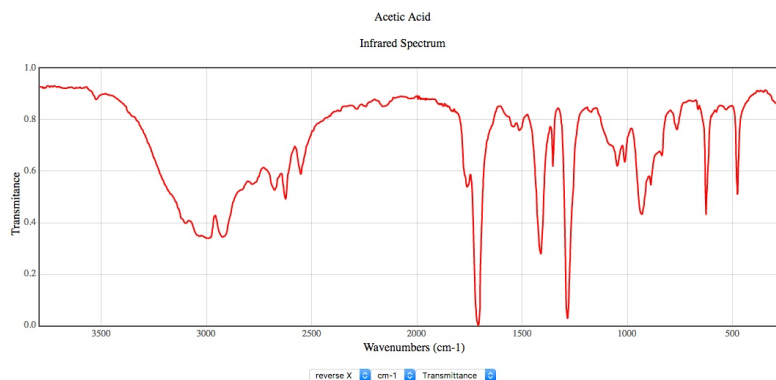
Ethanol



Ethanal = Acetaldehyde



Ethanoic Acid = Acetic Acid



You can see the “big bum” in the Ethanoic acid that the Ethanal does *not* have.

G1 The use of Ethanol in Alcoholic drinks

- Could you please look back at B1 in this Chapter and re-read all the things that I said about Fermentation/the killing of yeast (i.e. a living organism) when the Alcohol concentration of the solution that contains the yeast reaches 14-15% / the distillation of wines to produce spirits and the fortification of wines (such as sherry and port) with distilled Alcohols that have been produced by fermentation.
- **Methylated spirits** : Alcohol (in its generic sense) not only has industrial uses, but it can be very beneficial domestically e.g. as a solvent or it can be used in blow-torches for stripping old paint from wooden doors, etc. However, there is an enormous temptation for alcoholics to consume non-drinking Alcohols – therefore to make such Alcohols (e.g. methanol) unpalatable, producers of such Alcohols add substances that make the Alcohol smell and taste disgusting! Nobody in his/her right mind would want to drink “methylated spirits” (a non-drinking Alcohol produced for household purposes), but sadly those people who have become addicted to Alcohol DO drink the stuff and eventually they kill themselves! (If you are going to drink, then please drink moderately.)

G2 The use of Alcohols as a fuel

- You will remember that when we were talking about Fossil Fuels (Chapter 4 of the First Year book on Organic Chemistry) I told you that long straight-chained alkanes do not make high quality petrol because they explode too early i.e. they explode while they are in the *Compression* stage rather than in the *Explosion* stage (cf <http://www.schoolscience.co.uk/content/5/chemistry/catalysis/catsch3pg8.html>) of a Four-Stroke Automotive engine cycle – and I told you that short-chained alkanes/branched chain alkanes/and ring Carbon compounds make much better petrols. Well, the ultimate in short-chained alkanes is going to be a Carbon molecule that has only ONE Carbon atom in it i.e. methane. Methane would make a very good petrol – but unfortunately it cannot do so because Methane is a gas at room temperature and as soon as you put it into the tank of your car, it would escape out again!
- **Methanol as a fuel** : The Alcohol Methanol also has only one C atom in each of its molecules AND (because it is Hydrogen bonded) **it is a liquid** at room temperature and pressure! It therefore makes a superb additive to petrol (as indeed does Ethanol) – and it would be sensible for it to be used in petrol. However, Methanol attacks the metals in car engines VERY aggressively at high temperatures, and Methanol also attacks the central nervous system of animals (including human beings) and causes blindness, therefore Methanol as a petrol supplement is used only in racing cars. *In countries that do not have their own oil reserves, Methanol can be prepared from coal and it can then also be used in the preparation of “feedstock” (“feedstock” being the raw material from which plastics are made).*
- It is possible to use a combination of Methanol-and-an-Ether known as “MTBE” (methyl tertiary-butyl ether²⁶) $\text{CH}_3\text{--O--C}(\text{CH}_3)_3$ in petrol, and MTBE is made from Methanol and Isobutylene. Oil companies put MTBE into petrol because MTBE contains Oxygen and this increases the amount of Oxygen in the explosion and causes more complete combustion of the petrol. [More complete combustion increases fuel efficiency and reduces pollution.] However, MTBE is toxic and can spill onto the ground at petrol stations and then seep into underground water supplies – and that is why many governments ban the use of MTBE in petrols.
- **Ethanol as a fuel** : Short chained C molecules make very good (high octane) petrols. However, C1 to C4 **alkanes** are gaseous therefore (because they are not liquids at RTP) they cannot be used as petrol. C1 to C4 **Alcohols** are however hydrogen bonded **therefore they are LIQUIDS**, therefore they make good additives/ substitutes for petrol. This is particularly useful for those countries that do not have their own oil reserves but which can grow lots of sugar cane or palm oil, and also to a lesser extent beetroot/carrots/sugar maple/ etc, because all these vegetables/fruit can be turned into Ethanol – *but please be aware that Alcohols are less cost effective than alkanes as petrols because they emit less energy per volume of fuel than comparable alkanes.* It should also be noted that at high temperatures Ethanol attacks some of the metals in engines, therefore motor manufacturers have to allow for this when designing their engines. In addition, growing organic matter for fuel soothes the consciences of people in developed societies (while we drive around in our big gas-guzzlers) but it drives up the cost of food – and this hits poor people in developing countries **very VERY hard!** *Despite what you read in textbooks, there are very few easy solutions in real life.*

²⁶ Could you please try to draw the molecule. It really is very easy to do so.

G3 Alcohols as SOLVENTS

- You will remember that polar solvents dissolve polar substances, and that non-polar solvents dissolve non-polar substances. Well, Alcohols are very good solvents because they are both *polar* AND *non-polar* solvents! The hydroxy groups in the molecule are polar (and they form hydrogen bonds), and the alkyl parts of the molecules are non-polar.

G4 ANTIFREEZE

- I have (on page 7) already told you that the liquid that is put into the radiators of cars (*i.e. antifreeze*) is not water, but is distilled water mixed with either ethylene glycol (ethan-1,2-diol) or is distilled water mixed with a mixture of ethylene and propylene glycol (propan-1,2-diol) because the resulting mixtures have a lower freezing point than water and a higher boiling point than water. Water freezes at 0°C, but it **expands** between 4°C and 0°C,²⁷ and when it expands it does so with considerable force and this pushes apart the welded joints of a radiator – and the radiator then ceases to be watertight. In countries where the temperature drops below freezing point, water should therefore not be used by itself in the radiators of cars. Moreover, antifreeze has a much higher boiling point than water, therefore antifreeze also prevents radiators from boiling over in hot countries.
- On the next page I have drawn for you the “Information Tree” for Alcohols. Please learn to draw similar information trees that encapsulate on ONE piece of paper all the **important** information that you need to know about the reactions of whatever it is that you are studying in Chemistry or in any other subject. You will find information trees to be absolutely *invaluable* tools for learning e.g. you should construct your own information trees on Acids/Aldehydes/Ketones/etc – and you should then commit each tree to memory. Then when you get into the exam room you will know by heart all the reactions that you are required to know for the exam! In later life (e.g. if you go on and train to be a doctor²⁸) then your studies will be made immeasurably easier if you can encapsulate the information that you need into info-trees.

²⁷ Above 4°C water molecules flow easily around each other, but below 4°C the hydrogen bonds inside water **lock** all the molecules immovably into an expanded grid which occupies about 10% more space/volume than water – therefore ice has a greater volume than water (and is thus less dense than water).

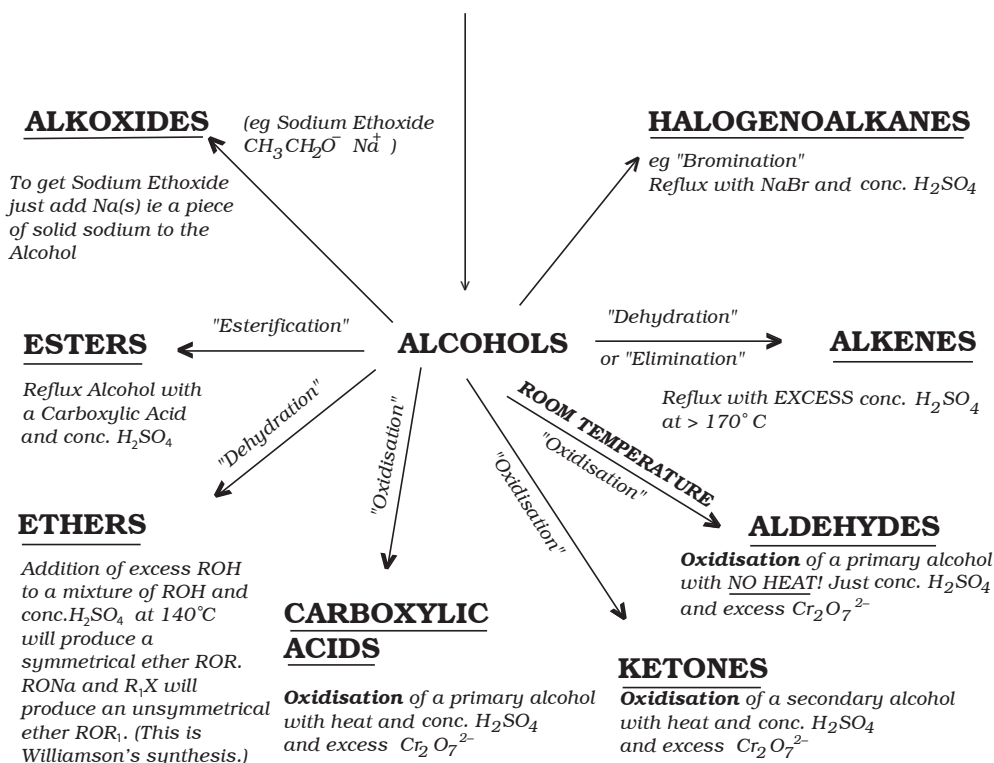
²⁸ Please note that there is nothing special about being a doctor or any profession. Society needs and should value the contribution of every human being. We could not function without dinner ladies/toilet cleaners/till checkout attendants/etc (and, for all I know, perhaps even lap-dancers). **Every single human being makes an important contribution to society.** No one human being makes a ‘better’ contribution than another. Brain surgeons and rocket scientists could not function without road sweepers/car mechanics/toilet cleaners/whatever.

Required reactions involving Alcohols for First Year 'A' Level Required reactions involving Alcohols for 'A' Level purposes

(page 13 onwards shows many of these reactions in greater detail)

AS Level methods of obtaining an alcohol

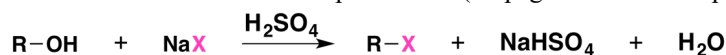
- 1) "Fermentation" of a sugar with yeast (as the catalyst).
- 2) "Hydration" of an alkene with steam (by electrophilic addition).
- 3) "Hydrolysis" of a halogenoalkane.



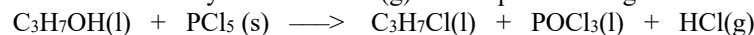
NB1 The **dichromate ion** is conventionally supplied by either Sodium or Potassium Dichromate. Please remember that Potassium Dichromate is carcinogenic. It is my understanding that the Cr^{6+} ion is quickly transformed into the Cr^{5+} ion and it is *that* which is corrosive and dangerous. **Do make sure that you dispose of your reactants appropriately!**

NB2 The **Dehydration Reactions of Alcohols** result in their conversion into alkenes, and involves the elimination of a molecule of water. Dehydration requires the presence of an acid as the catalyst and the application of heat. When transforming an Alcohol into an Alkene, there must be an excess of **CONCENTRATED Sulphuric Acid!** If an excess of the **Alcohol** is used, then an **ether** will be produced. To transform the Alcohol into an Alkene, the temperature must be at least 170°C .

NB3 **Halogenation of an Alcohol**: Alcohols react with strongly acidic hydrogen halides viz. HCl and HBr, and HI (*but the reaction of a primary Alcohol and $\text{HCl}(\text{aq})$ is very slow at RTP*). **Alcohols do NOT react with nonacidic NaCl, NaBr, or NaI.** Chemistry LibreTexts (written by Jim Clark) points out that primary and secondary Alcohols can be converted to alkyl chlorides and bromides by allowing them to react with a mixture of a sodium halide and concentrated sulphuric acid (cf. page 12 of this Chapter).



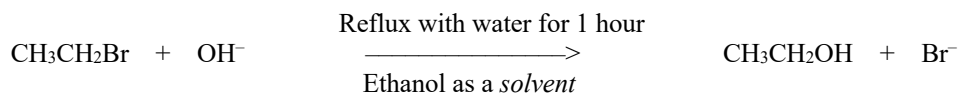
NB4 One of the classic tests for an Alcohol is to react it with phosphorous pentachloride, PCl_5 , whereupon the characteristic white fumes of hydrochloric acid(g) will be produced e.g.



Hydrolysis and Hydration

Hydrolysis (I believe that “lysis” in ancient Greek means “to cut/to break/to unbind”)

- In Organic Chemistry there can be confusion between the terms Hydration and Hydrolysis (because they both refer to the reaction whereby an “H” and an “OH” species from Water add onto a molecule). In Hydration, an “H” and an “OH” species **add onto** a molecule, whereas in Hydrolysis a molecule is **split into two new species** by the action of the Water as it reacts with the molecule. An example of Hydrolysis would be

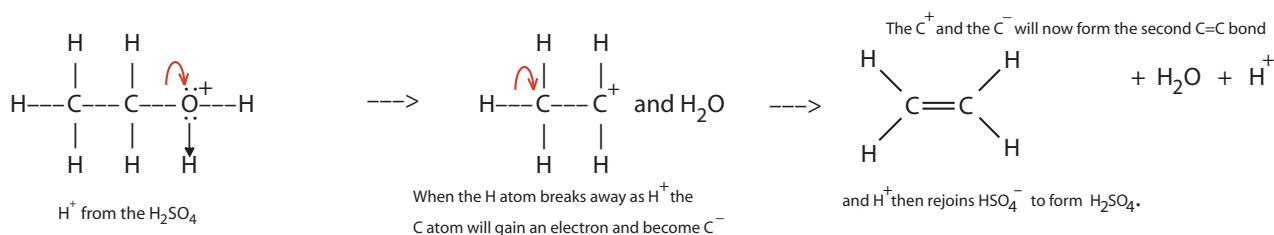


Hydration

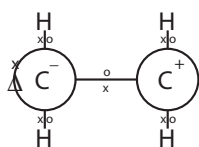
- In contrast, in “Hydration” both the water molecule and the substance with which it reacted form ONE new compound e.g. Ethene and Water react to form Ethanol.



- Since this constitutes an addition reaction, clearly **Hydration can take place only with an unsaturated molecule** (such as ethene).
- That is almost the end of the Chapter on Alcohols, but I am now going to ask you a question and I want you to answer it truthfully.
- In the right hand diagram at the top of page 14 I said that “the C^+ and the C^- will now form the second $\text{C}=\text{C}$ bond”, and the question that I want to ask you is: *did you understand what that meant, or did you just read it and not make any attempt to understand it?* Be honest.
- I repeat the diagram here, and if you did not do so before, then could you please now try to work out exactly what I was referring to when I said that “the C^+ and the C^- atoms will now form the second $\text{C}=\text{C}$ bond”.

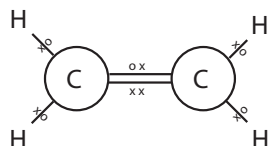


- The answer is that



In the diagram alongside, the C atom on the left has gained an electron (ie the Δ one left behind by the H atom) and has therefore become C^- , while the C atom on the right has lost an electron, therefore it has become C^+ . In other words, the C atom on the left instead of having FOUR electrons now (briefly) has FIVE electrons in its outermost shell. (If you count the crosses and the Δ you will see that this is so.) **This is a totally unstable situation therefore something has to happen.**

and,

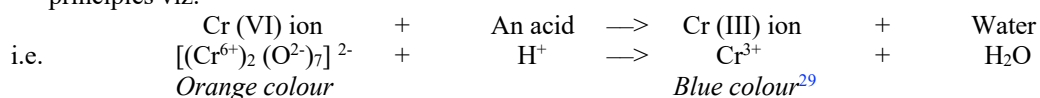


The C^- atom ie the one with the extra electron (making five electrons in its outer shell) now uses two of those five electrons to form a dative bond with the C^+ atom (ie the one that is short of one electron thus having only three electrons in its outer shell). **The second bond is thus now formed!** Both the C atoms now have four electrons in their outermost shells, therefore neither of them now has a charge. (The fact that one of the electrons originally came from an H atom is not relevant.)

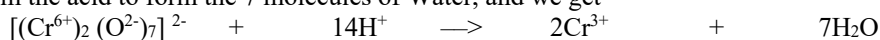
- Whenever you see a C^+ single bonded to a C^- , then you can take it that a second bond will form.
- I want you to get into the habit of thinking about everything that you encounter. This is a very good habit to develop, and it will save you a lot of problems later on in your lives. A junior doctor who was once looking after my very sick wife carried out a procedure that he did not fully understand – and instead of asking the consultant exactly what was going on, he just went ahead and fudged it and very nearly killed my wife! She forgave him, but (30 years later) I still have not done so.
- Do you remember that I put an Appendix at the end of Chapter 33 of “Foundation Chemistry”? Well, here it is again on the next page. At that time I said that you would not understand what you were reading but that you would do so when you came to Alcohols in “Chains & Rings”. Well, now you can read it again and understand every single word of it!

APPENDIX

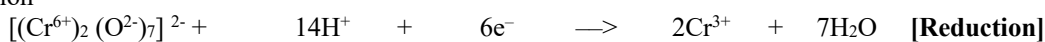
- An Alcohol can be oxidised into an Aldehyde/a Carboxylic Acid/or a Ketone depending on what sort of Alcohol it is and what the reaction conditions are. Whatever happens, an oxidising agent in conjunction with concentrated sulphuric acid **must** be used – and *the Sulphuric Acid is here NOT acting as a catalyst (because during the oxidation reaction, the sulphuric acid will here convert both the sodium and the chromium ions into sulphates)*. The $\text{Cr}_2\text{O}_7^{2-}$ Chromium (VI) Dichromate ion is normally used as the oxidising agent and it can come from either Sodium Dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). Let us, for the purposes of this exercise, use Sodium Dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), concentrated Sulphuric Acid (H_2SO_4) and Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and let us start by considering the operation from first principles viz.



- Here there are two “ Cr^{6+} ” species on the LHS of the equation, therefore we need “ 2Cr^{3+} ” species on the RHS of the equation. The 7 O atoms on the LHS of the equation will form 7 molecules of water and we need **14** protons from the acid to form the 7 molecules of Water, and we get

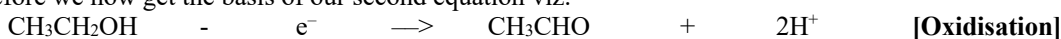


- We now need to balance **the charges** in the equation because on the LHS of the equation they add up to “12” i.e. “ $2 \times (+6) + 7 \times (-2) + 14 \times (+1)$ which gives 12”], whereas on the RHS of the equation they add up to “6” [i.e. “ $2 \times (+3)$ ”].
- There are therefore 6 too many positive charges on the LHS of the equation, and if we were to **ADD 6 (negative) electrons** to the LHS of the equation, then this would REDUCE the positive charge on the LHS of the equation by “6” because each electron has a single negative charge! We therefore get “ $(-2 + 14) + (-6) = 12 - 6 = 6$ ” on the LHS and “ $2 \times (+3) = 6$ ” on the RHS, and this gives us our first half-equation

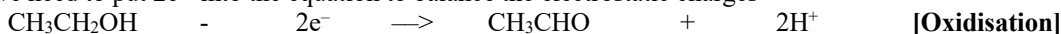


In the process of Oxidising the Alcohol, the Chromate ion is reduced.

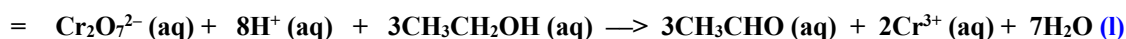
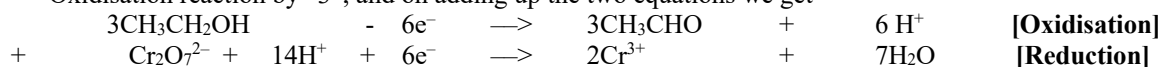
- When a Primary Alcohol is converted into an Aldehyde two H^+ species are ejected, and since there must be an Oxidation reaction to balance the Reduction reaction, the Alcohol has to lose at least one electron therefore we now get the basis of our second equation viz.



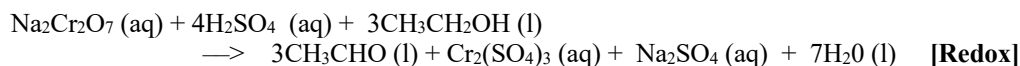
but we need to put 2e^- into the equation to balance the electrostatic charges



- Lastly, in order to balance the number of electrons in the two Redox equations we must multiply the Oxidation reaction by “3”, and on adding up the two equations we get



and when we insert the spectator ions (where 4H_2 is the equivalent of 8H) we get



Isn't that just beautiful. You use your brains and you solve a complicated problem easily! If you have understood what I have said on this page, then you are qualified to do an entrance exam for Oxford/Cambridge/Harvard/Yale/MIT or anywhere in the world.

²⁹ As I have said before, in Physics you will have learnt that when something that is blue is mixed with something that is orange, then the resulting mixture appears green – and it is precisely the colour change from **orange** to **green** that tells us that this reaction is taking place.

A BIT ABOUT COLOUR CHANGES

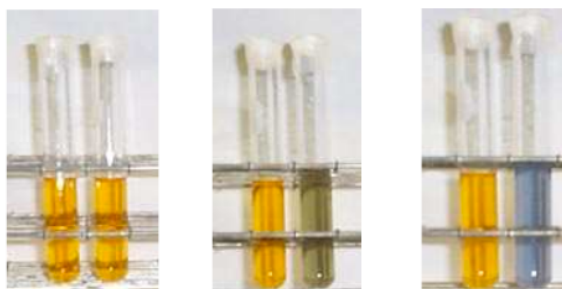
(Orange to green, and is it blue or is it yellow)

- If you are using Potassium as the cation for your source of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions as the oxidising agent when oxidising an Alcohol, then you need to know the colour change from orange to green.
- Potassium dichromate powder (the one on the left below) has a bright orange colour (but to me it is more red than orange!) and potassium chromate (CrO_4^{2-}) powder has a bright yellow colour.



Source: https://en.wikipedia.org/wiki/Chromate_and_dichromate

- When you perform the oxidation of an Alcohol using **acidified** dichromate ions (it will not work without a very strong concentrated acid) in a test-tube, then you get the following colour changes



Source: <https://projects.ncsu.edu/project/chemistrydemos/Organic/Breathalyzer.pdf> (North Carolina State University)

- The initial colour change is orange to green (because there is still orange present and blue plus orange looks green). When all the Alcohol has been oxidised (and remember you must use an excess of acidified dichromate ions otherwise there is a danger that you will not complete the reaction that you have set out to observe), then the colour will be blue. That is the basis of the orange to green claim. It is actually orange to blue – but in life you must know which battles to fight and which you cannot win. The examiners do NOT want to hear orange to blue, they want to hear orange to green – **so give them what they want to hear.**
- This Chapter has exercised your grey matter so why don't you watch a nice little video on https://www.youtube.com/watch?v=_jypU3FvS_o
- It shows you some nice colour changes. The stuff that you see in the video is all about the colour changes that can be observed when you move the dynamic equilibrium to the right or to the left.