

Name:

Organic Chemistry	Objectives
22. Types of Reactions in Organic Chemistry	<p><u>Addition Reactions</u></p> <ul style="list-style-type: none"> <li>-explain what is meant by an addition reaction</li> <li>-write balanced equations using structural formula for the reactions of the alkenes with hydrogen, chlorine, bromine, water and hydrogen chloride</li> <li>-outline the industrial importance of:               <ul style="list-style-type: none"> <li>• products of the addition reactions of ethene with chlorine, bromine, water and hydrogen chloride</li> <li>• hydrogenation of vegetable oils</li> </ul> </li> <li><b>-describe the mechanisms of ionic addition (addition of HCl, Br<sub>2</sub>, Cl<sub>2</sub>, only to ethene)</b></li> <li><b>-describe the evidence for this mechanism as: the reaction of ethene with bromine water containing sodium chloride results in the formation of 2-bromoethanol 1-bromo-2-chloroethane and 1,2-dibromoethane</b></li> <li>-explain what is meant by addition polymerisation</li> <li>-outline the polymerisation reaction of ethane and propene (reaction mechanism not required).</li> <li>-account for the unreactivity of benzene with regard to addition reactions relative to ethene</li> <li>-account for the use of alkenes as raw materials in the industrial manufacture of plastics</li> <li>-outline the range and scope of the petrochemical industry</li> <li>-list two synthetic products of the petrochemical industry (structures not required unless specified elsewhere on the syllabus)</li> </ul> <p><u>Substitution Reaction</u></p> <ul style="list-style-type: none"> <li>-define substitution reaction</li> <li>-recognise halogenation of alkanes as a substitution reaction</li> <li>-write balanced equations using structural formula for the halogenations of alkanes</li> <li><b>-describe the mechanism of free radical substitution (monochlorination of methane and ethane only)</b></li> <li><b>-discuss the evidence for the mechanism of free radical substitution</b> <ul style="list-style-type: none"> <li>• use of ultraviolet light even for a very short period causes a chain reaction</li> <li>• formation of trace quantities of ethane and butane in the monochlorination of methane and ethane, respectively</li> <li>• these reactions are speeded up by the addition of a known source of free radicals, such as tetraethyllead</li> </ul> </li> <li>-explain what is meant by esterification</li> <li>-explain what is meant by base hydrolysis of esters</li> <li>-write balanced equations using structural formulas to illustrate base hydrolysis of esters</li> <li>-prepare a sample of soap (structures of reactants and products required)</li> <li>-discuss the manufacture of soap (structures of reactants and products required)</li> </ul> <p><u>Elimination Reactions</u></p> <ul style="list-style-type: none"> <li>-explain what is meant by an elimination reaction</li> <li>-explain what is meant by a dehydration reaction</li> <li>write balanced equations using structural formula for the dehydration of alcohols</li> </ul> <p><u>Redox Reactions</u></p>

	<p>-write balanced half equations using structural formula for the oxidation (using <math>\text{KMnO}_4</math> or <math>\text{Na}_2\text{Cr}_2\text{O}_7</math>) of:</p> <ul style="list-style-type: none"> <li>• alcohols to (i) aldehydes and (ii) acids</li> <li>• aldehydes to acids</li> </ul> <p><b>-carry out calculations involving percentage yield of ethanal (the balanced equation will be given)</b></p> <p>-demonstrate the properties of ethanal (limited to reactions with (i) acidified potassium manganate(VII) solution, (ii) Fehling's reagent and (iii) ammoniacal silver nitrate)</p> <p>-relate the production of ethanal to the metabolism of ethanol in the human body</p> <p><b>-carry out calculations involving percentage yield of ethanoic acid (the balanced equation will be given)</b></p> <p>-carry out diagnostic tests on ethanoic acid (limited to reactions with sodium carbonate, magnesium and <b>ethanol</b>)</p> <p><b>-account for the lower susceptibility of ketones than aldehydes to oxidation</b></p> <p><b>-write balanced equations using structural formulas for the reduction of carbonyl compounds using a <math>\text{H}_2/\text{Ni}</math> catalyst</b></p> <p>-recall that combustion is a reaction common to most organic compounds</p> <p>-recall that the fully halogenated alkanes are non-flammable, relate this property to their use in flame retardants and fire extinguishers</p> <p>-oxidise phenylmethanol (benzyl alcohol) to benzoic acid using potassium permanganate under basic conditions.</p> <p>-recall that benzaldehyde is a constituent of almond kernels (structure of benzaldehyde not required)</p> <p>-purify a sample of benzoic acid by recrystallisation outline the use of melting point to confirm purity determine the melting point of benzoic acid</p> <p><u>Reactions as acids</u></p> <p>-write balanced equations using structural formulas for the reactions of alcohols with sodium</p> <p><b>-account for the acidic nature of the carboxylic acid group</b></p> <p>-write balanced equations using structural formulas for the reactions of carboxylic acids with magnesium, with sodium hydroxide and with sodium carbonate</p> <p><u>Organic synthesis: principles and examples</u></p> <p>-recall that chemical synthesis involves (i) bond breaking and (ii) bond forming</p> <p>-describe the organic synthesis of PVC from ethene (structures and synthetic route not required)</p> <p><b>-work out reaction schemes of up to three conversions recalling familiar reactions</b></p>
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### ADDITION REACTIONS

*Def<sup>n</sup>*: An **addition reaction** is one in which two substances react to form a single substance.

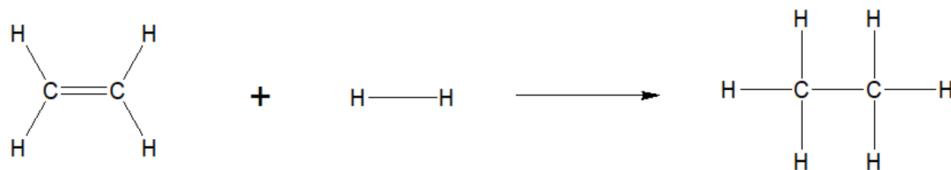
General Notes on add<sup>n</sup> reactions:

1. Always will occur on a double/triple bond.
2. Geometry will change from planar (unsaturated C-C bonds) to tetrahedral (saturated C-C bonds).
3. Benzene does not undergo addition reactions as its delocalised electrons make it very stable and unreactive.

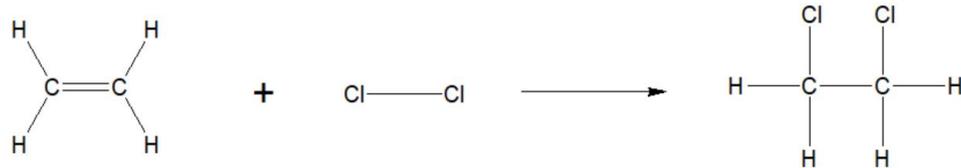
Uses of add<sup>n</sup> reactions:

1. Hydrogenation of vegetable oils. Forms margarine.  $\text{H}_2$  (with Ni catalyst) added to unsaturated oils to partially saturate them. This is also a *reduction* reaction as we are adding hydrogen.
2. Polymerisation reactions to make long chains of carbons we call plastics.

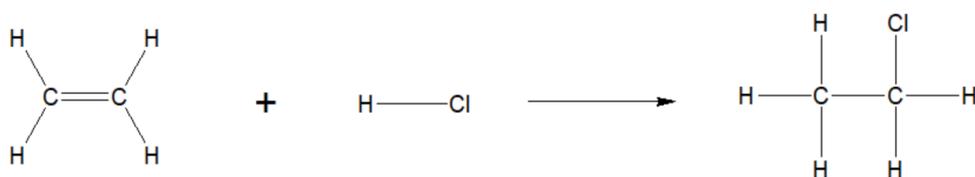
Ethene is often seen as the most important organic chemical, as it undergoes many addition reactions to form different organic compounds. Example we need to know are:



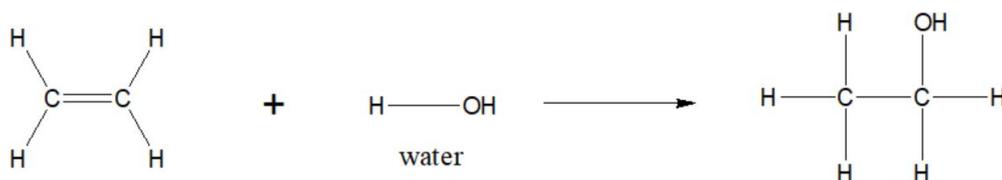
Ethane



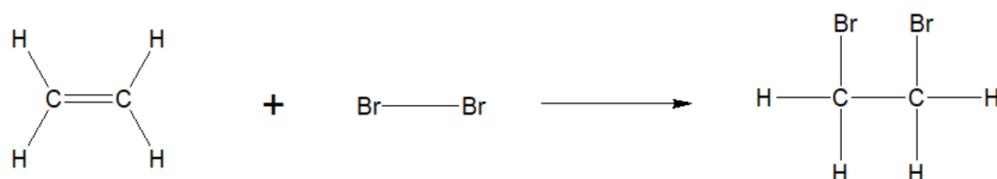
1,2-dichloroethane



Chloroethane



ethanol

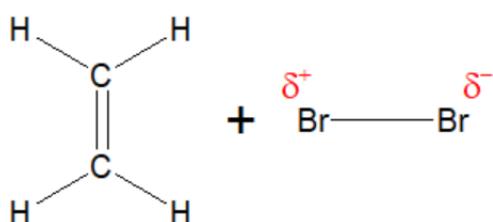


1,2-dibromoethane

The last example, called the **Bromination of Ethene** needs to be study in more detail. We need to know the *mechanism* of the reaction: Overall this type of reaction is known as **Ionic Addition**.

*Def<sup>n</sup>*: The **mechanism** of a reaction is the detailed step-by-step description of how the reaction occurs.

### Step 1: Polarisation

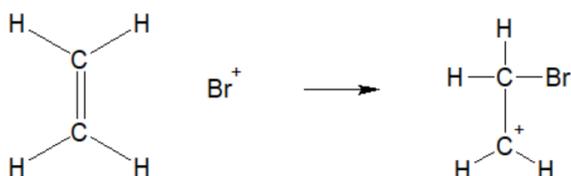


The C=C double bond in ethene has a high concentration of negative charge.

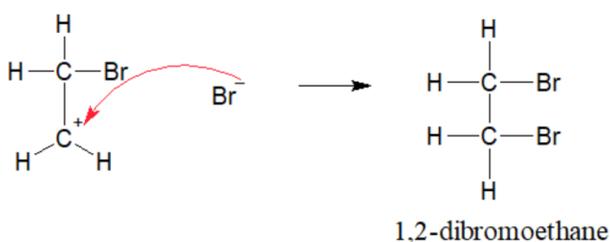
As the Br<sub>2</sub> approaches the ethene, the electrons are repelled away from the ethene, polarising the Br<sub>2</sub>.

**Step 2: Heterolytic Fission:**

The polarisation eventually becomes so great, the molecule splits into  $\text{Br}^-$  and  $\text{Br}^+$ . We call this heterolytic fission because the  $\text{Br}^-$  took all 2 electrons from the Br-Br bond.

**Step 3: Carbonium Ion Formation:**

The  $\text{Br}^+$  attacks the electron rich C=C double bond. This forms a carbonium ion (positive charge on C)

**Step 4: Ionic Attack**

The  $\text{Br}^-$  ion attacks the carbonium ion, forming 1,2-dibromoethane.

**Evidence for this mechanism:**

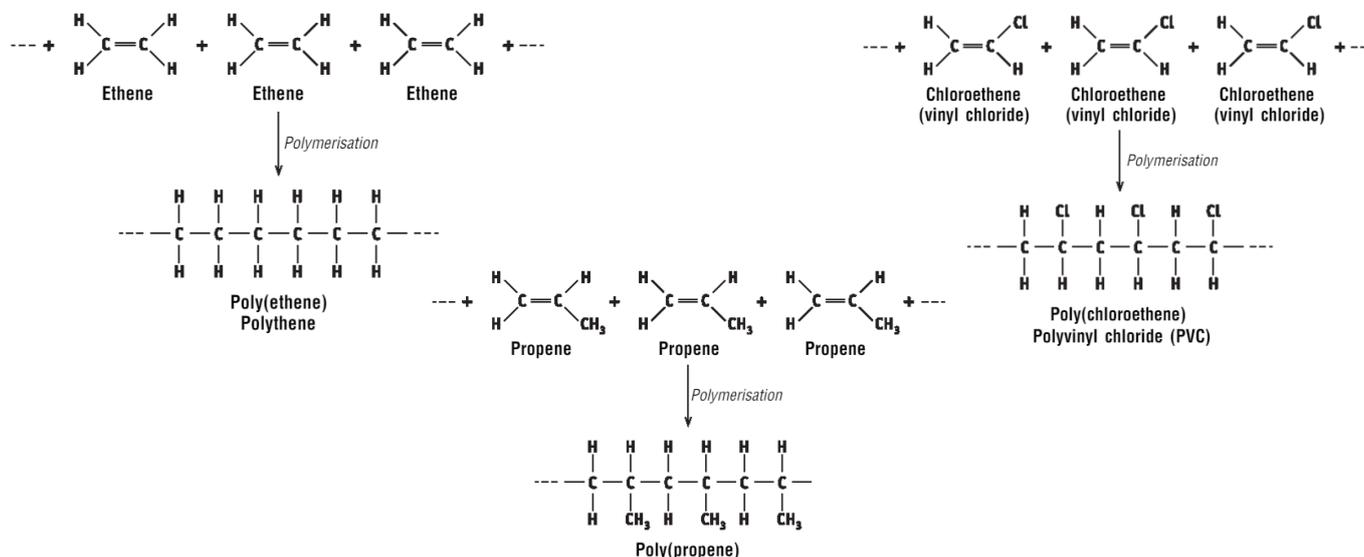
If this reaction is carried out in bromine water with some  $\text{Cl}^-$  ions added, we see the normal 1,2-dibromoethane product being formed, but two other products form also; 1-bromo-2-chloroethane and 2-bromoethanol. These form because of the  $\text{Cl}^-$  or the  $\text{OH}^-$  (from water's self-ionisation) can replace the  $\text{Br}^-$  in step 4.

TO WRITE THE MECHANISM FOR THE ADDITION OF  $\text{Cl}_2$  OR  $\text{HCl}$ , SIMPLY REPLACE THE  $\text{BR}_2$ !

**Polymerisation** reactions are also a type of addition reaction.

*Def<sup>n</sup>*: **Polymers** are long chain molecules made by joining many small molecules (monomers).

Polymers are made up of many repeating units.

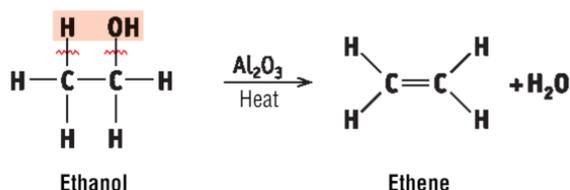


## ELIMINATION REACTIONS

*Def<sup>n</sup>*: An **elimination reaction** is one in which a small molecule is removed from a larger molecule, leaving a double bond on the larger molecule.

General Notes on elim<sup>n</sup> reactions:

1. Geometry changes from tetrahedral to planar as a double bond is formed.
2. Generally involved the removal of a water molecule (H<sub>2</sub>O) – these are also called *dehydration* reactions.



This example is the reaction you carried out when producing ethene gas. Notice that water is removed from the ethanol.

Know that Al<sub>2</sub>O<sub>3</sub> and heat is used to remove water in a dehydration reaction.

## SUBSTITUTION REACTIONS

*Def<sup>n</sup>*: A **substitution reaction** is one in which an atom (or group of atoms) in a molecule is replaced with another atom (or group of atoms).

There are 2 main types we study:

### 1. Halogenation of Alkanes

This involves substituting hydrogen atoms in alkanes with halogens (F, Cl, Br, I, etc.).

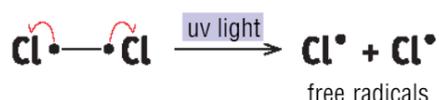
Fully halogenated alkanes e.g. CCl<sub>4</sub> are used as flame retardants. Less common now as they damage the ozone layer.

We need to know the overall reaction, and the detailed mechanism for the *monochlorination of methane/ethane*.

The mechanism for the monochlorination of methane is shown below.

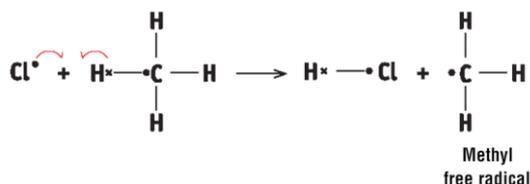
This mechanism is called **free-radical substitution**.

*Step 1: Homolytic Fission*



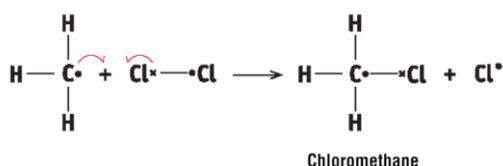
UV light is used to break the Cl-Cl bond. Each Cl atom receives 1 of the 2 electrons from the bond. This forms 2 Cl radicals which are very reactive.

*Step 2: Propagation*



One of the Cl radicals attacks the methane molecule to form HCl and a methyl radical.

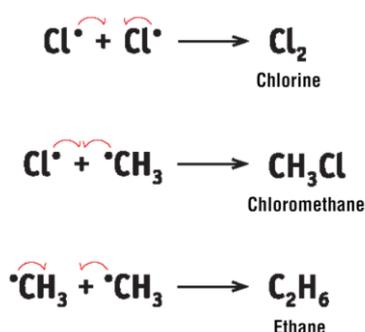
*Step 3: Propagation*



The methyl radical attacks a new Cl<sub>2</sub> molecule to form a molecule of chloromethane and a Cl radical.

The Cl radical now undergoes Step 2 again, and this forms a chain reaction between Steps 2 and 3.

## Step 4: Termination



When most of the reactants have been used up during Steps 2 and 3, there are only a small number of Cl radicals and methyl radicals left over. These combine to form Cl<sub>2</sub>, chloromethane and ethane.

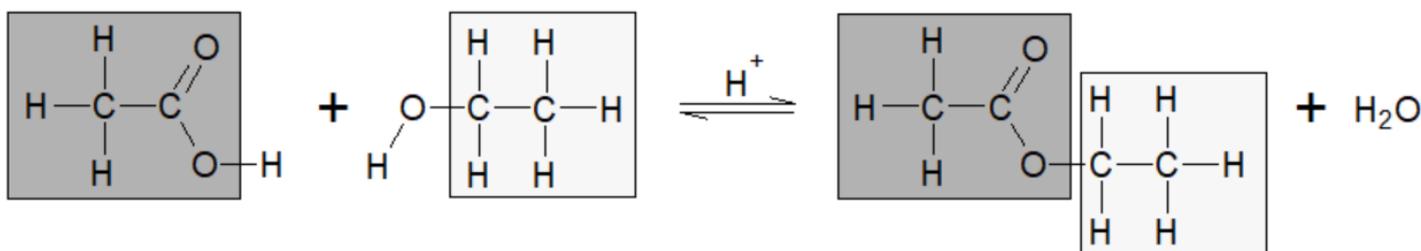
Note: The mechanism for the monochlorination of **ethane** is identical. Practice writing it out. The *italics* shown in the table below refer to the evidence for the monochlorination of ethane.

## Evidence for this mechanism:

Evidence	Explanation
Reaction takes place when exposed to UV light	Suggests a free-radical mechanism whereby Cl <sub>2</sub> is broken down into Cl radicals.
For every photon of UV light used, thousands of chloromethane molecules are formed	Suggests a chain reaction is involved.
Ethane is found in the products ( <i>butane</i> )	Methyl ( <i>ethyl</i> ) radicals must have been present, as ethane ( <i>butane</i> ) forms when two methyl radicals combine.
Adding tetramethyllead ( <i>tetraethyllead</i> ), which is a source of free radicals, increases the rate of the reaction	Only a reaction which uses free radicals would be sped up by adding free radicals.
Addition of an inhibitor, like O <sub>2</sub> , slows down the reaction	Shows a chain reaction is taking place, as O <sub>2</sub> combines with free radicals, stopping the chain reaction.

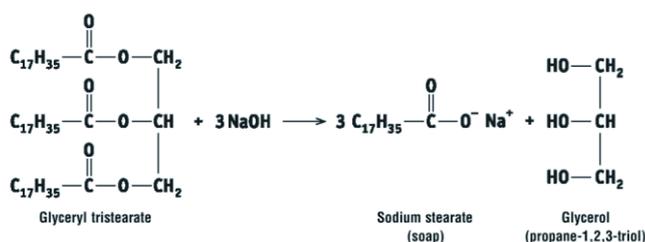
## 2. Esterification

When a carboxylic acid is reacted with an alcohol (with a small amount of H<sub>2</sub>SO<sub>4</sub> as a catalyst), an ester is formed. This is a substitution reaction as the H on the –OH of the carboxylic acid has been substituted with an alkyl (methyl-, ethyl-, etc.) group.



Notice that this is an equilibrium reaction. This means that the reverse reaction can also occur. To do this, we simply need to add water. This is called *hydrolysis*.

Hydrolysis of esters can also be carried out using a base e.g. NaOH or KOH. This results in the formation of the sodium/potassium salt of the carboxylic acid. These salts are known to us as **soaps**. This process of *base hydrolysis* is also called **saponification**. You carried out this reaction when you prepared a sample of soap:



## How does soap work?

Soap molecules contain a long, non-polar carbon chain which will dissolve oils (e.g. from skin). The opposite end of the molecule contains a polar COO<sup>-</sup>Na<sup>+</sup> which will dissolve salts from sweat and will also dissolve in water. This allows soap to pick up oils and salts and then be washed down the drain.

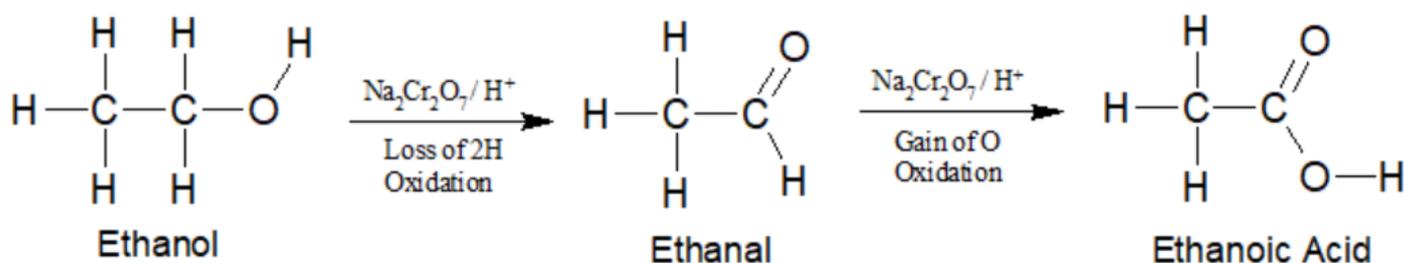
**REDOX REACTIONS**

General Notes on redox reactions:

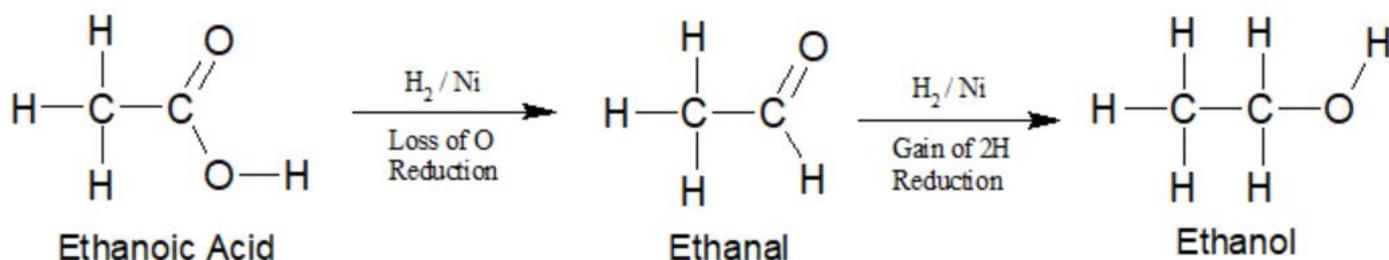
- Oxidation is the addition of O or the removal of H.
- Reduction is the removal of O or the addition of H
- Oxidation carried out using either:
  - Acidified Sodium Dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ) Cr(VI) [orange] gets reduced to Cr(III) [green].
  - Acidified Potassium Permanganate ( $\text{KMnO}_4/\text{H}^+$ ) Mn(VII) [purple] gets reduced to Mn(II) [colourless].
- Reduction is carried out using Hydrogen gas and a Nickel catalyst ( $\text{H}_2/\text{Ni}$ )

**Primary Alcohols**

Primary alcohols get oxidised to aldehydes. If there is excess oxidising agent present, the aldehydes can then be further oxidised to carboxylic acids.



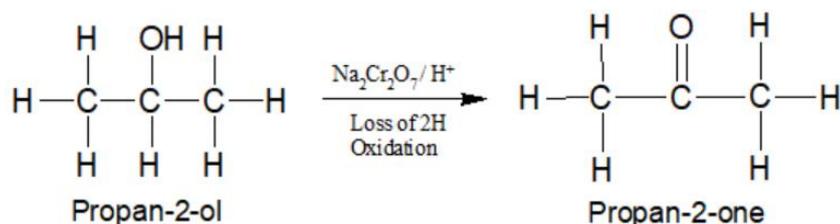
Carboxylic acids get reduced to aldehydes. If there is excess reducing agent, the aldehydes can be further reduced to alcohols.



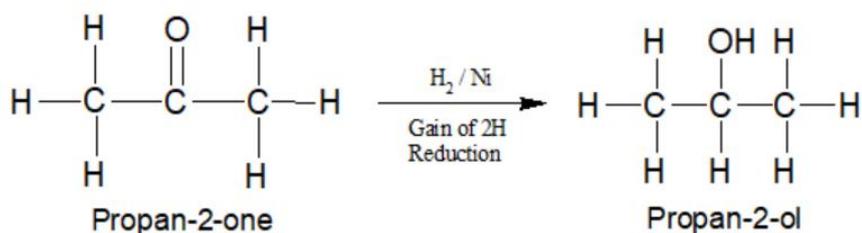
Note that all of the changes happen at the terminal carbon (the carbon at the end), where the oxygen atom was.

**Secondary Alcohols**

Secondary alcohols get oxidised to ketones. They cannot be oxidised any further. This is because the carbon with the oxygen is not at the end of the molecule. Thus we form a ketone rather than an aldehyde. As carboxylic acids can only have the COOH on the terminal carbon, a ketone can never be oxidised to a carboxylic acid.



Ketones get reduced to secondary alcohols.



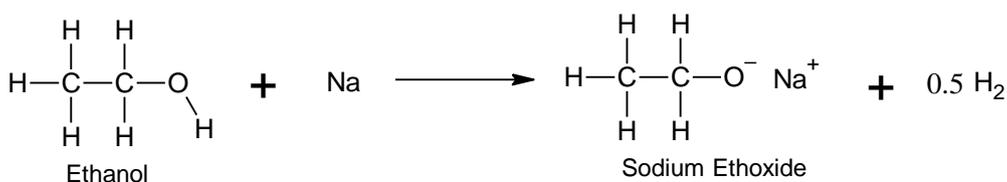
### Organic Redox reactions in everyday life

1. A bottle of wine left open to the air will start to taste “vinegary” after some time. This is because oxygen in the air oxidises the ethanol in the wine to ethanoic acid.
2. When ethanol is consumed, the liver works hard to break it down, as it is a foreign toxin to the body. The liver oxidises the ethanol to ethanal, which is even more toxic! The ethanal is what causes some of the bad symptoms of a hangover. Eventually, when given enough time, the ethanal is further oxidised by the liver to carbon dioxide and water, which are excreted through the lungs and urine.
3. Old-style breathalysers (these can still be bought in your local pharmacy!) contained potassium dichromate crystals [Cr(VI) - orange]. If alcohol was in a person’s system and they breathed through a tube containing the crystals, the ethanol in the breath would be oxidised. This would reduce the Cr(VI) [orange] to Cr(III) [green], showing that ethanol was present.

## REACTIONS AS ACIDS

### Alcohols reacting with Sodium

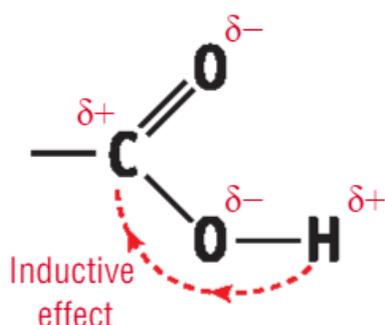
The H on the –OH of an alcohol can act as an acid when reacted with the *extremely* reactive metal, sodium. This forms the sodium salt of the alcohol, and hydrogen gas.



### The Acidic nature of the Carboxylic Acids

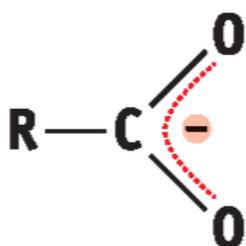
Why is the H on the –COOH group acidic (why can it dissociate)? There are 2 reasons:

1. Inductive effect



Because the O in the C=O is very electronegative, the C is left with a slight positive charge. This draws electron density towards the C and away from the –OH, allowing the H to dissociate.

## 2. Stability of the carboxylate ion



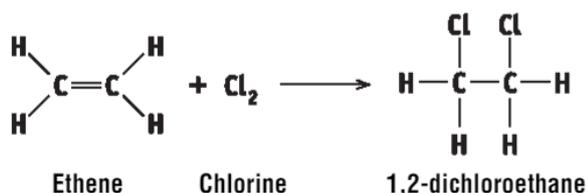
When the H of the  $\text{-OH}$  dissociates to form a  $\text{H}^+$  we are left with a carboxylate ion  $\text{-COO}^-$ . The negative charge is not localised to just one of the oxygens and is instead delocalised between the two of them. This delocalised structure gives the carboxylate ion extra stability, allowing the  $\text{H}^+$  to easily dissociate.

**Common reactions with carboxylic acids:**

- Acid + Base  $\rightarrow$  Salt + Water  
e.g.  $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$
- Acid + Carbonate  $\rightarrow$  Salt + Carbon Dioxide + Water  
 $2\text{CH}_3\text{COOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{CH}_3\text{COONa} + \text{CO}_2 + \text{H}_2\text{O}$
- Acid + Metal  $\rightarrow$  Salt + Hydrogen  
 $2\text{CH}_3\text{COOH} + \text{Mg} \rightarrow (\text{CH}_3\text{COO})_2\text{Mg} + \text{H}_2$

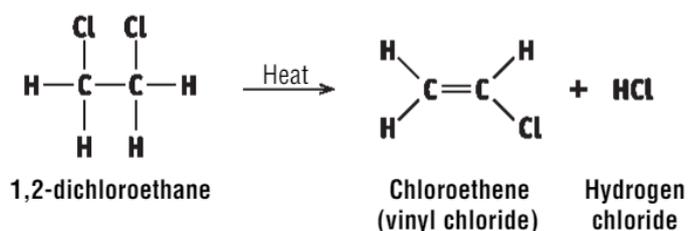
**SYNTHESIS OF PVC FROM ETHENE**

Step 1:



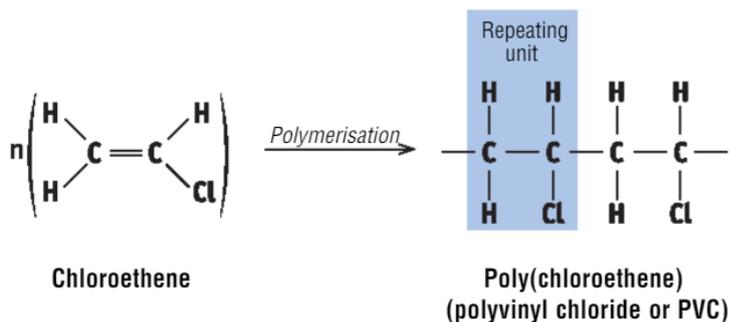
Ethene and chlorine react to form 1,2-dichloroethane. (Addition reaction of which we know the mechanism)

Step 2:



Heat is used to thermally crack the 1,2-dichloroethane into chloroethene and HCl.

Step 3:



The chloroethene undergoes a polymerisation reaction to form polychloroethene (PVC)