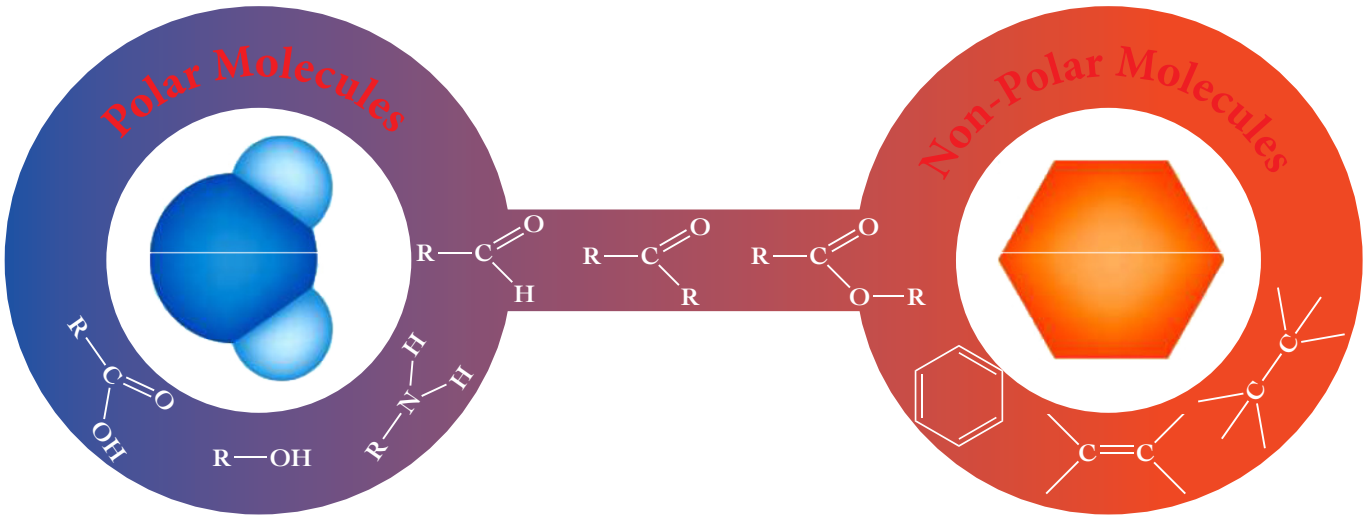
Higher Chemistry

Unit 2:

Nature's Chemistry

Student:



Topic 5

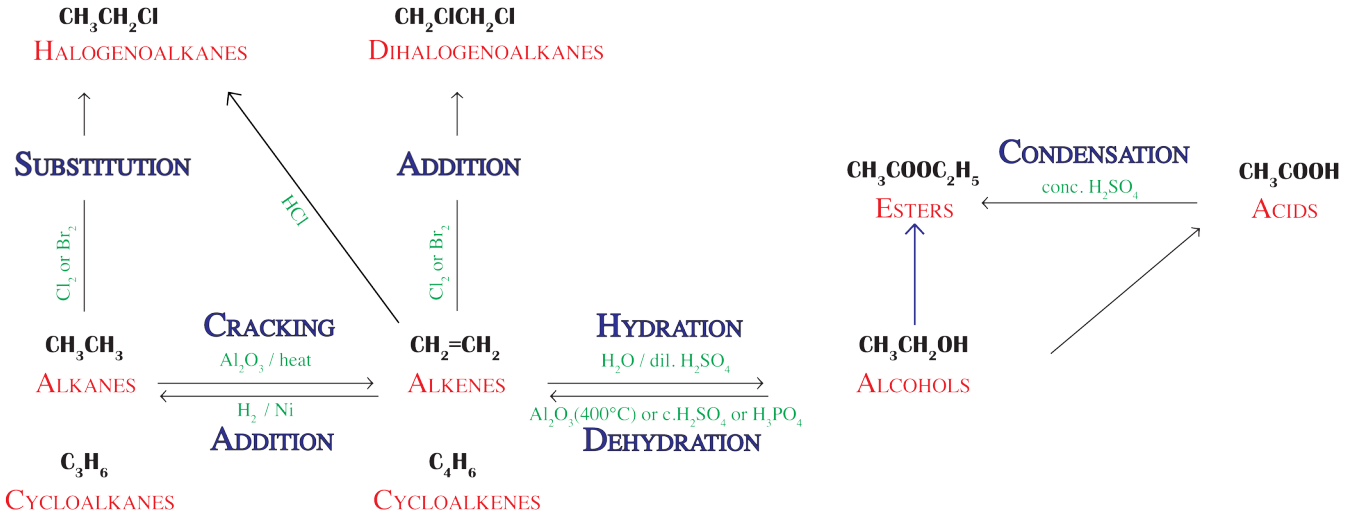
Systematic Organic in Context
Structures & Naming
Oxidation Reactions
Antioxidants

5.1 Systematic Organic in Context

This first lesson topic takes an overview of the Organic reactions met in this and previous courses and some of the contexts in which these reactions are met.

Previous Chemistry

This activity examines the systematic approach to the reactions met in previous courses.



Learn:

- ***Names - RULES for naming !***
- ***Structures*** of both reactant molecule and product molecule
- ***Title*** of the reaction
- ***Reagents*** used to carry out the reaction

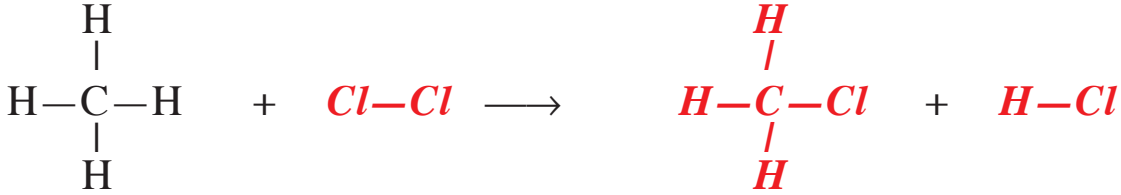
Substitution - an *atom* or *group* will be ***removed*** from a normally ***saturated*** molecule to allow a ***different*** *atom* or *group* to take its place.

Normally, the product formed is also ***saturated*** and ***2*** ***reactant*** molecules react to form ***2*** ***product*** molecules

Equation using systematic names:

methane + ***chlorine*** ⟶ *chloromethane* + ***hydrogen chloride***

Equation using full structural formulae:



Equation using shortened structural formulae:

$$CH_{4(g)} + Cl_{2(g)} \longrightarrow CH_3Cl_{(g)} + HCl_{(g)}$$

Cracking - a *larger* ***saturated*** molecule is *broken apart* to produce *smaller* molecules, at least one of which will be ***unsaturated***.

Normally, a ***catalyst*** will be used. Sometimes only a couple of *neighbouring* ***hydrogen*** atoms will be '*cracked*' off to produce a single ***unsaturated*** product. This reaction can also be called ***elimination***.

Equation using systematic names:

propane ⟶ *propene* + ***hydrogen***

Equation using full structural formulae:

Equation using shortened structural formulae:

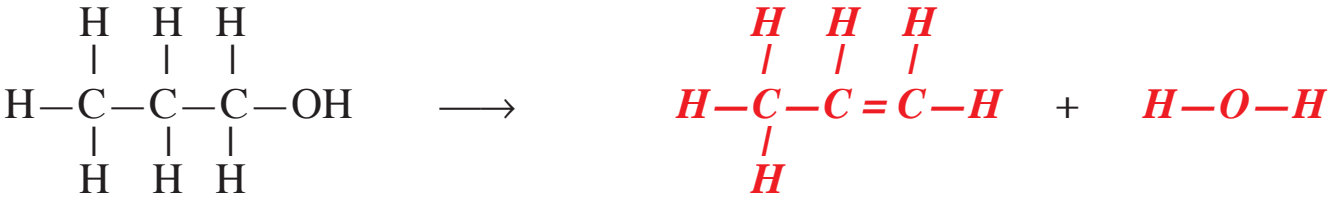
$CH_3CH_2CH_{3(g)} \longrightarrow CH_3CHCH_{2(g)} + H_{2(g)}$

Dehydration - a specific ***elimination*** reaction in which *neighbouring* ***hydrogen*** atom and ***hydroxyl*** group (—OH) will be '*cracked*' off to produce an ***unsaturated*** product. The eliminated atoms form a stable ***water*** molecule.

Equation using systematic names:

propan-1-ol ⟶ *propene* + ***water***

Equation using full structural formulae:



Equation using shortened structural formulae:

$CH_3CH_2CH_2OH_{(l)} \longrightarrow CH_3CHCH_{2(g)} + H_2O_{(l)}$

Elimination is the reverse reaction to ***addition***.

Addition - a small molecule reacts with an ***unsaturated*** molecule and adds *across* the ***double*** bond to make a ***saturated*** product.

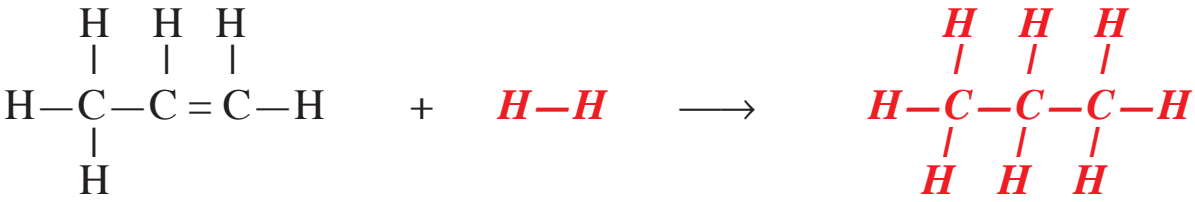
Many different molecules can be added and many of these reactions have their own names.

Hydrogenation - addition of ***hydrogen***

Equation using systematic names:

propene + *hydrogen* $\xrightarrow{\text{Ni } catalyst}$ ***propane***

Equation using full structural formulae:



Equation using shortened structural formulae:

$$CH_3CHCH_{2(g)} + H_{2(g)} \longrightarrow CH_3CH_2CH_{3(g)}$$

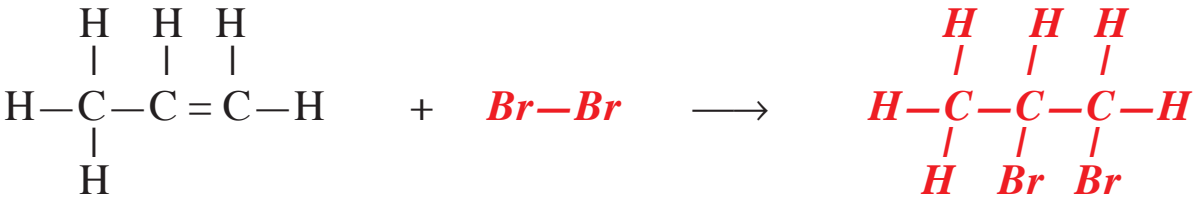
Hydrogenation is mainly used to convert *highly* ***unsaturated oils*** into *more* ***saturated fats***. E.g. *vegetable oil* can be thickened and solidified to make *margarine* by ***hydrogenation***.

Halogenogenation - addition of ***halogen***

Equation using systematic names:

propene + ***bromine*** $\longrightarrow$ ***1,2-dibromopropane***

Equation using full structural formulae:



Equation using shortened structural formulae:

$$CH_3CHCH_{2(g)} + Br_{2(g)} \longrightarrow CH_3CHBrCH_2Br_{(l)}$$

The ***addition*** reaction with a ***halogen***, usually ***bromine***, remains the accepted test for ***unsaturation*** - the presence of a C = C ***double*** or C ≡ C ***triple*** bond.

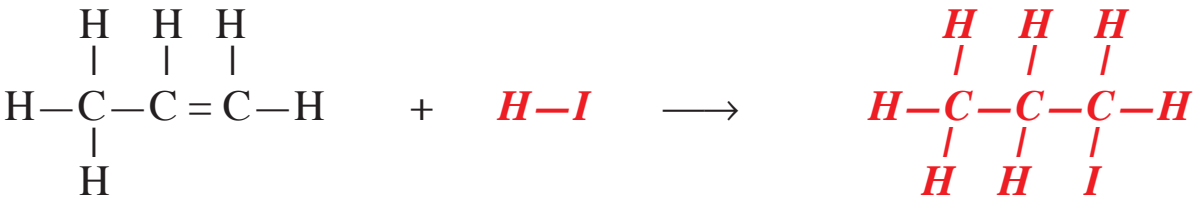
The ***halogen*** is decolourised ***bromine***, ***orange*** $\longrightarrow$ *colourless*
chlorine, ***green*** $\longrightarrow$ *colourless*
iodine, ***brown*** $\longrightarrow$ *colourless*

Hydrohalogenation - addition of ***hydrogen halide***

Equation using systematic names:

propene + *hydrogen iodide* ⟶ ***1-iodopropane***

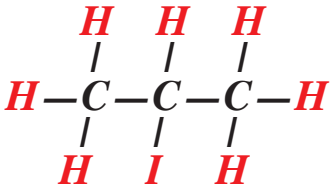
Equation using full structural formulae:



Equation using shortened structural formulae:

$$CH_3CHCH_{2(g)} + HI_{(g)} \longrightarrow CH_3CH_2CH_2I_{(l)}$$

Hydrohalogenation is an alternative when only ***one halogen*** atom is wanted on the product molecule. Depending on the position of the ***double bond***, however, more than one ***isomer*** is possible. In the above example, *2-iodopropane* is another possible product.

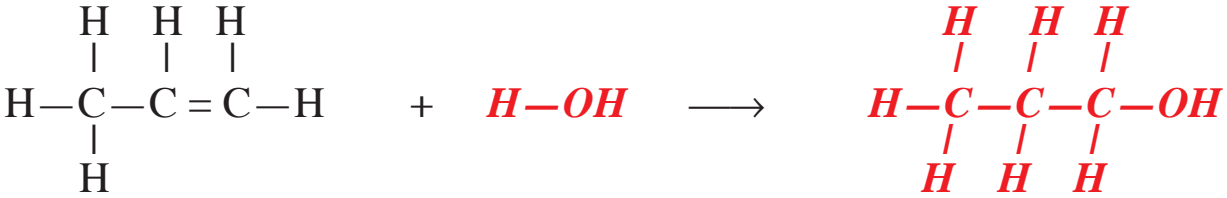


Hydration - addition of ***water***

Equation using systematic names:

propene + ***water*** ⟶ ***propan-1-ol***

Equation using full structural formulae:

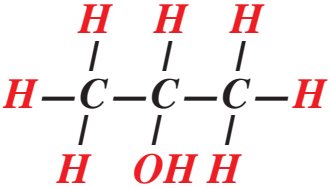


Equation using shortened structural formulae:

$$CH_3CHCH_{2(g)} + H_2O_{(l)} \longrightarrow CH_3CH_2CH_2OH_{(l)}$$

Hydration of an ***alkene*** is an important method for making *alcohols* but, like the previous example, more than one product can be formed.

In this case, the second ***isomer*** would be *propan-2-ol*.



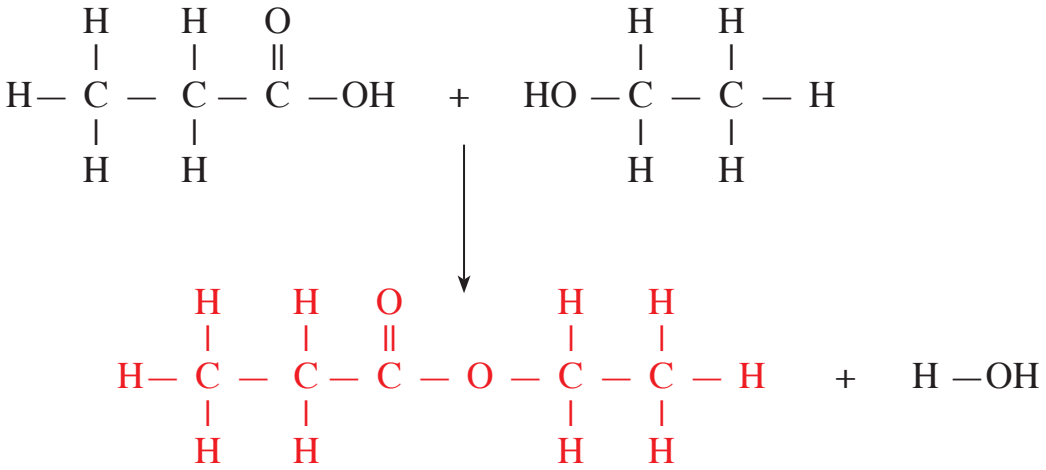
Propan-1-ol is a ***primary alcohol*** while *propan-2-ol* is a ***secondary alcoho***l. The significance of these labels will become clearer in later lessons.

Condensation - two smaller molecule react to ***join together*** and form a larger molecule, ***eliminating*** a *small stable molecule*, usually ***water*** through one molecule losing ***an —H atom*** whilst the other molecule loses ***an —OH*** (*hydroxyl*) group.

Equation using systematic names:

propanoic acid + *ethanol* ⟶ ***ethyl propanoate***

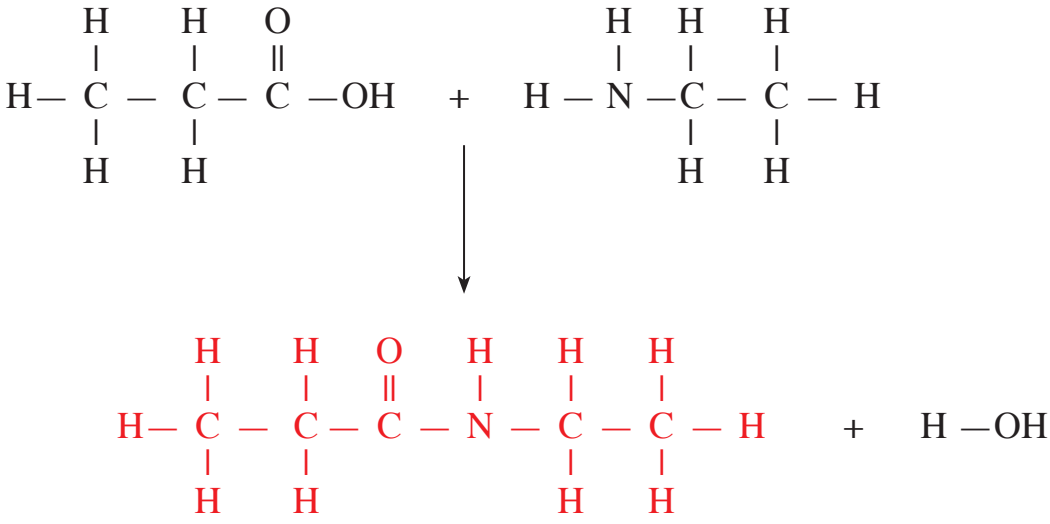
Equation using full structural formulae:



Equation using shortened structural formulae:

$$CH_3CH_2COOH_{(l)} + \boldsymbol{CH_3CH_2OH_{(l)}} \longrightarrow \boldsymbol{CH_3CH_2COOCH_3CH_{2(l)}}$$

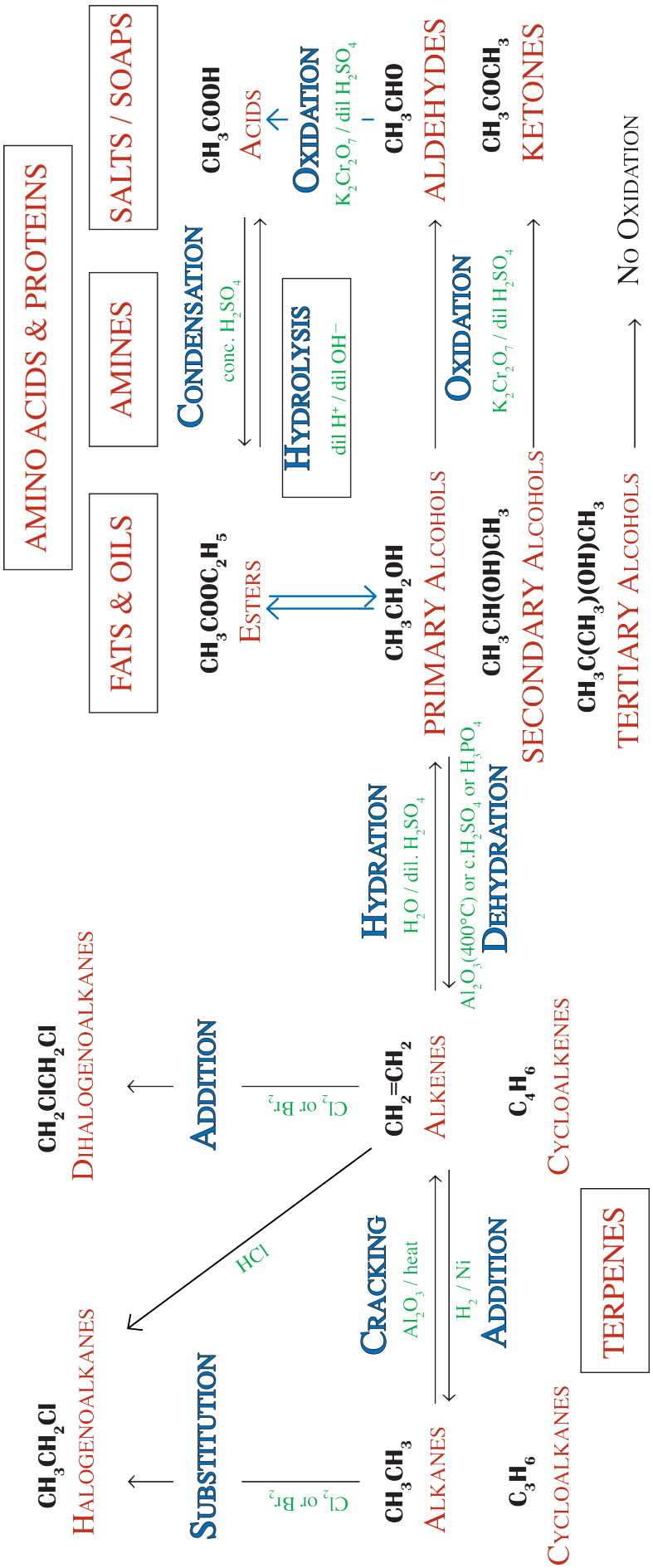
The other main ***condensation*** reaction that you will meet will involve an *acid* reacting with an *amine* to form an *amide*. This is very similar to the *ester* forming reaction above.



This is the reaction used to ***join*** many *amino acids* together to form *proteins*.

New Chemistry

This activity looks at some of the new reactions / families that you will meet in this Unit.



Much of the new Chemistry revolves round learning ***Oxidation*** in more detail.

As can be seen, there are 3 types of ***Alcohols*** to be learnt and they have different products - ***Aldehydes*** or ***Ketones***, or none - when oxidised.

Aldehydes are the intermediates formed when a ***Primary Alcohol*** is oxidised to eventually form an ***Acid***.

Condensation becomes even more important - along with the reverse reaction, ***Hydrolysis***.

Not just ***Esters*** are formed by a ***Condensation*** reaction - ***Proteins*** and ***Fats & Oils*** are also formed by ***Condensation*** and broken down by the ***Hydrolysis*** reaction.

Soaps are the ***Salts*** of *Fatty Acids* formed when ***Alkali Hydrolysis*** is done to a ***Fat*** or ***Oil***.

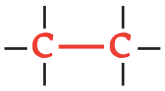
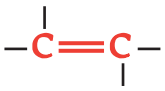
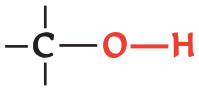
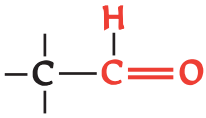
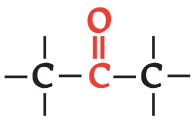
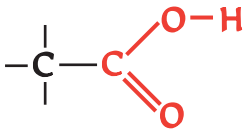
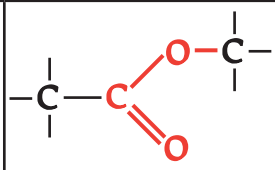
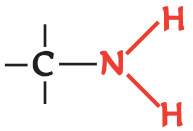
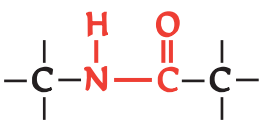
Terpenes are natural *hydrocarbons*, found mainly in plants, formed by joining together smaller molecules called ***isoprene***,

2-methylbuta-1,3-diene.

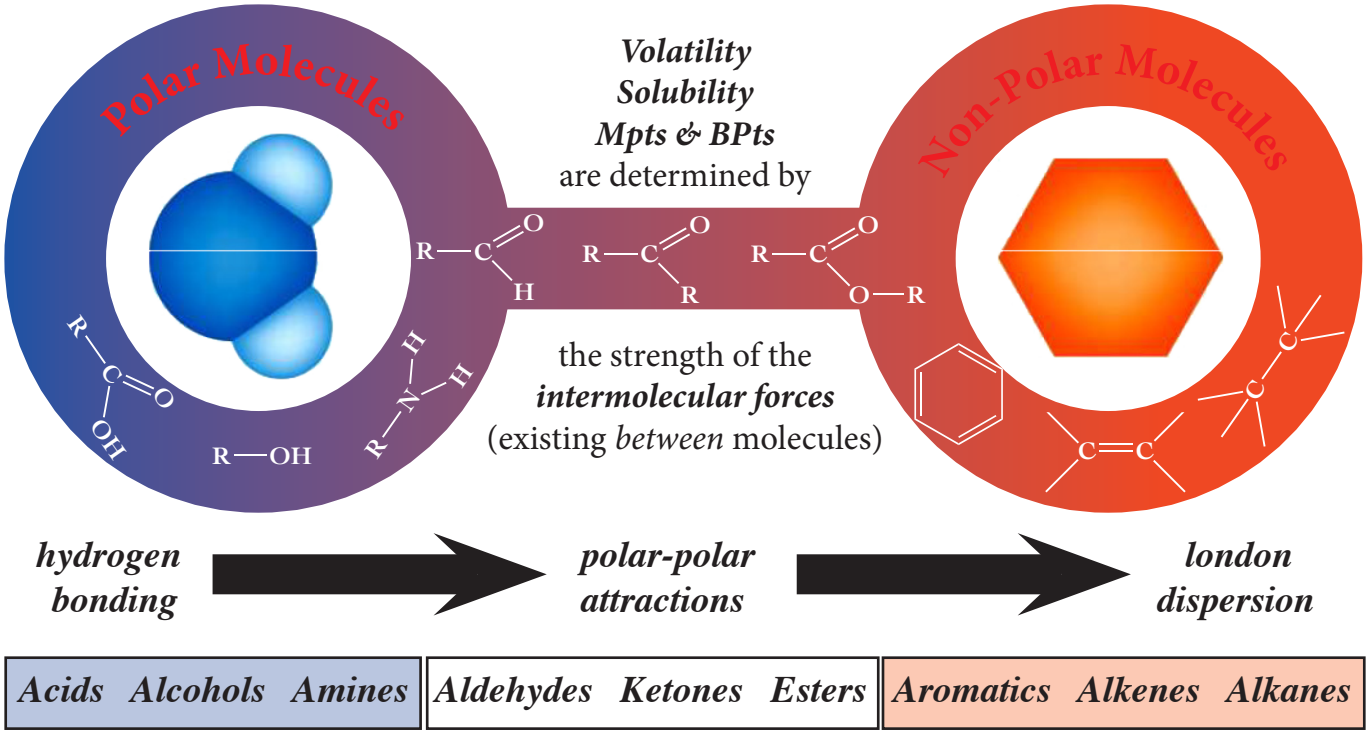
Terpenes belong to a group of chemicals usually referred to as *essential oils* which should not be mixed up with *edible oils* (***Fats & Oils***) and *mineral oils* derived from *Crude Oil* and made by the *Petrochemical* industry.

Functional Groups & Properties

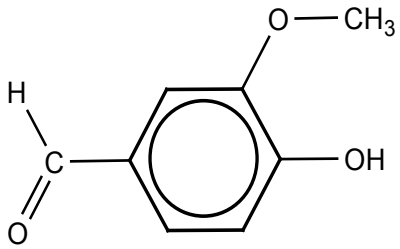
This activity explains the functional groups found in these molecules and their possible effect on the chemical and physical properties of the molecule.

Family Name	*Functional Group*	*Name of Group*	*Chemical Reactions*	*Intermolecular Forces*	*Solubility in Water*
alkane		carbon to carbon single	substitution	london dispersion forces	insoluble
alkene		carbon to carbon double	addition	london dispersion forces	insoluble
alcohol		hydroxyl group	oxidation condensation	hydrogen bonding	very soluble
aldehyde		carbonyl group	oxidation	polar-polar	limited solubility
ketone		carbonyl group	none	polar-polar	limited solubility
acid		carboxyl group	condensation	hydrogen bonding	very soluble
ester		carboxylate group	hydrolysis	polar-polar	insoluble
amine		amino group	condensation	hydrogen bonding	very soluble
amide		amide link	hydrolysis	hydrogen bonding	only small amides soluble

As well as determining their ***Chemical Reactions***, ***Functional Groups*** can also effect the ***Physical Properties***. Properties such as



For example, the *vanilla bean* produces a compound called *vanillin*, which is used as a flavouring additive in sweet foods such as ice cream.



Vanillin

This molecule has effectively, 4 ***functional groups***:-

The ***benzene ring*** and the *ether* group (—O—CH_3) are dealt with in *Advanced Higher*.

The ***hydroxyl*** group (—OH) and the ***carbonyl*** group (—CH=O) will be expected to be learnt well this year.

Within the same molecule there can be ***non-polar groups*** such as the ***aromatic benzene*** ring, whilst the *ether* and ***aldehyde*** (***carbonyl***) are ***slightly polar***.

Probably the most influential group will be the ***very polar hydroxyl*** group which is capable of ***hydrogen bonding*** and may make this molecule ***water soluble***.

Context - Kitchen Chemistry

This activity demonstrates how much of the Organic Chemistry met in this Unit will be taught within the context of Kitchen Chemistry

Flavour

Most of our 'tasting' is done through our noses, so most flavour molecules are*volatile* (*weak intermolecular forces*) such as

esters - many have sweet fruity smells - e.g. '*pear drops*' - *pentyl ethanoate*
aldehydes - can however be ***oxidised*** over time resulting in (sometimes unpleasant) changes in flavour
terpenes - '*essential oils*' are responsible for many distinctive flavours such as *cinnamon* and *ginger* as well as *oranges* and *lemons*.
acids - such as *vinegar*, *ethanoic acid* are used to introduce 'sour' flavours

Cooking

Cooking can *dissolve* out the flavour molecules so whilst many foods can be safely *cooked in water,* others are better *cooked in oil*.

Cooking also effects the structure of, in particular, ***proteins*** which can result in significant change in the *texture* of certain foods during cooking.

Texture

Protein *structure* has an important impact on the *texture* of food and can be effected by *changes in temperature* (*cooking*) and *changes in pH* (*marinading* in ***acids*** such as *vinegar*, *ethanoic acid*).

Foods, such as curries, often '*separate*' into '*water layer*' and '*oil layer*' as a result of *differences in solubility* (*different intermolecular forces*).

Colour

Colour can arise in many ways but larger ***terpenes*** are often responsible for the *yellow*, *orange* or *red* colour of so many foods - e.g. *carotene* in carrots.

Energy

Whilst ***carbohydrates,*** our main '*energy food*', are not covered in this course, ***proteins*** also contribute energy whilst *fats & oils* are our most concentrated source of energy.

Additives

antioxidants - can be added to food, though many foods already contain *Vitamin C* - a natural *antioxidant*

emulsifying agents - are used to prevent '*water layers*' and '*oily layers*' from separating. These molecules are often made from ***fats & oils*** and behave in exactly the same way as *soap molecules*. *Milk* contains natural ***emulsifiers***.

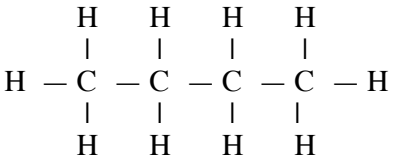
In addition, many reactions triggered by *UV light*, such as the ***substitution*** reaction between *alkanes* and *bromine*, involve the production of ***free radicals***. ***Free radicals*** start ***chain reactions*** which are responsible for the ageing of your skin. *Sun cream* contains chemicals designed to absorb UV before it reaches your skin.

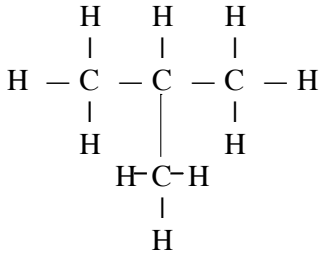
Vitamin E and *melatonin* are natural ***free radical scavengers*** that can help counter the effect of free radicals. Many ***cosmetic*** products contain *free radical scavengers* which react with ***free radicals*** to form stable molecules and prevent ***chain-reactions*** starting.

5.2 Naming Molecules

This lesson largely revises the principles behind naming and how they can be applied in more complex molecules

Naming Alkanes





This activity deals with how to name branched alkanes using systematic names, i.e. names that follow a very definite system which is based on the structure of the molecule.

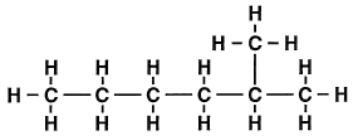
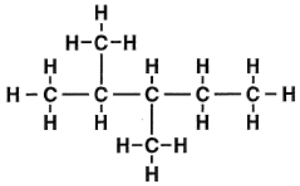
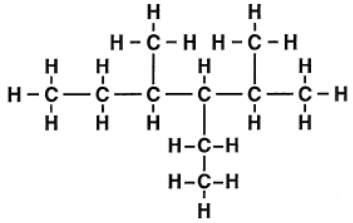
In a ***straight-chain*** *hydrocarbon*, all the ***carbon*** atoms in the molecule are linked one after the other in a ***single*** continuous chain.

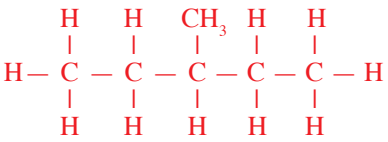
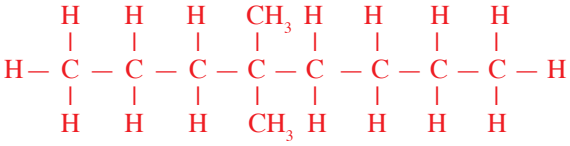
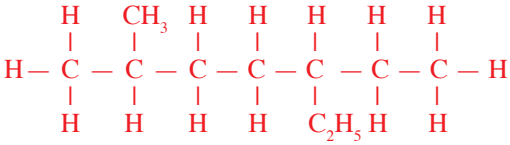
In a ***branched-chain*** *hydrocarbon*, the molecule has one or more ***side chains*** of carbon atoms off the main chain.

Due to ***branching***, it is possible to have *different* ***structural*** arrangements for the *same* ***molecular*** *formula*. ***Butane***, C_4H_{10}, has two *different* structures called ***isomers***. Clearly both of them cannot have *exactly* the same name.

Naming Rules for Alkanes

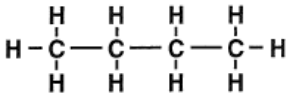
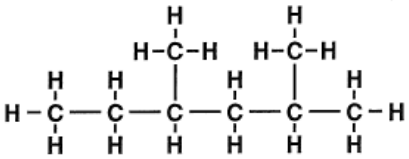
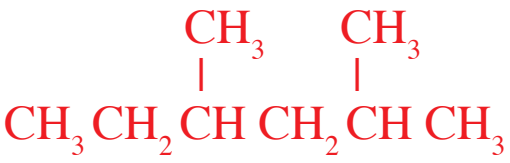
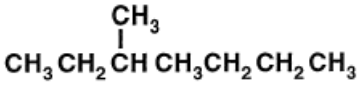
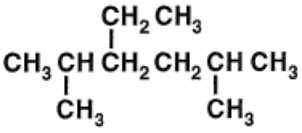
1. The ***longest chain*** defines the main chain and the last part of the name
2. ***Numbering*** of the main chain starts from the end that gives the lower overall number positions for side branches
3. ***Side branch*** names end in ***'-yl'*** and depend on the number of carbon atoms in them: *methyl* for 1 carbon, *ethyl* for 2 carbon atoms, *propyl* for 3 carbon atoms, etc.
4. ***Alphabetical*** order is used if different side branches appear in the same structure (*ethyl* before *methyl*).
5. ***Hyphens*** are used before or after numbers that come next to letters within a name (2-ethyl-3-methyl..)
6. ***Commas*** are used between numbers showing more than one of the same side branch (2,2,3-trimethyl..)

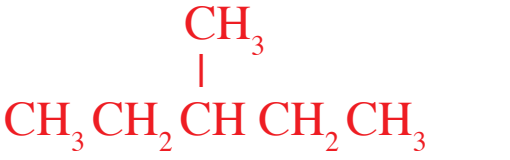
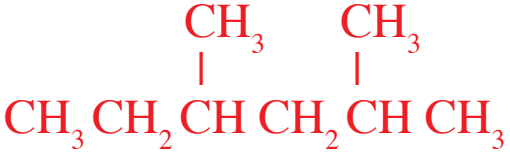
Full structural formula	*Systematic name*
	2-methylhexane
	2,3-dimethylpentane
	3-ethyl-2,4-dimethylhexane

Systematic name	*Full Structural formula*
3-methylpentane	
4,4-dimethyloctane	
5-ethyl-2-methylheptane	

Shortened Structural Formulae

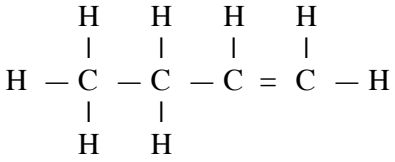
This activity is about writing and using shortened structural formulae for alkanes

Full Structural Formula	*Shortened Structural Formula*
	$CH_3CH_2CH_2CH_3$
	
Shortened Structural Formula	***Systematic Name***
	3-methylheptane
	3-ethyl-2,4-dimethylhexane

Systematic Name	*Shortened Structural Formula*
3-methylpentane	
2,4-dimethylhexane	

Branched Alkenes

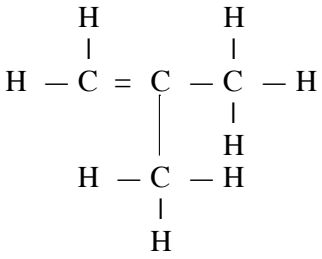
This activity considers how to use systematic names to indicate both the positions of side branches and the position of the double bond in the alkene structure.



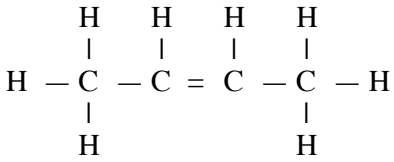
but-1-ene

There are even more ***isomers*** possible in the *alkene* family. Again there are ***straight****-chain alkenes* and ***branched****-chain alkenes*.

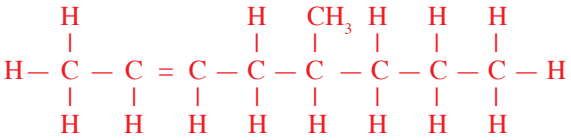
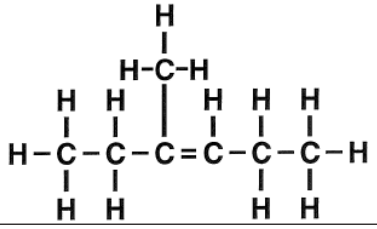
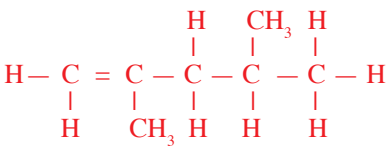
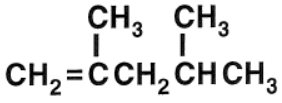
In addition, it is possible to change the ***position*** of the ***double*** *bond* to introduce even more *different* ***structural*** *formulae*.



2-methylprop-1-ene

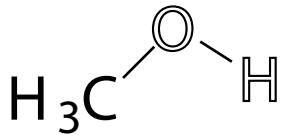


but-2-ene

Branched Alkene Structures	
Name:	5-methyloct-2-ene
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH=CHCH_2CH(CH_3)CH_2CH_2CH_3$
Name:	3-methylhex-3-ene
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2C(CH_3)=CHCH_2CH_3$
Name:	2,4-dimethylpent-1-ene
Full Structural Formula:	
Shortened Structural Formula:	

Alkanols

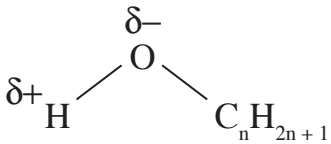
This activity revises the alkanol family



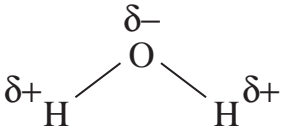
$C_n H_{2n+1} OH$

The ***functional group*** in alkanols is the ***Hydroxyl*** *group*.

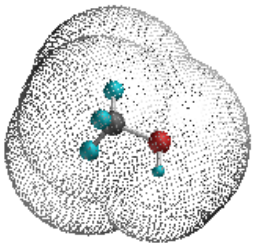
The ***alkanols*** can be thought of as '*substituted alkanes*' - a ***hydrocarbon*** chain with the ***hydroxyl*** *group* replacing one of the ***hydrogen*** atoms.

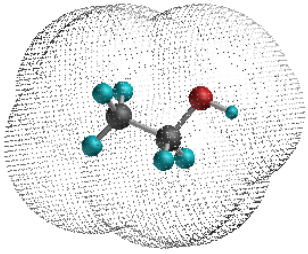


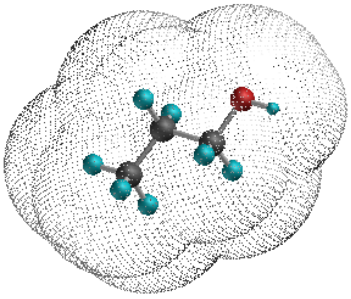
Like ***water***, *alkanols* are ***covalent*** molecules and, as a result, are *very poor* ***conductors*** of electricity.



Like ***water***, *alkanols* have a ***polar*** O—H bond which allows ***hydrogen*** *bonding* between molecules. As a result, water and smaller alkanols will '*dissolve*' in each other as the ***strength*** of their *intermolecular* forces are very ***similar***.





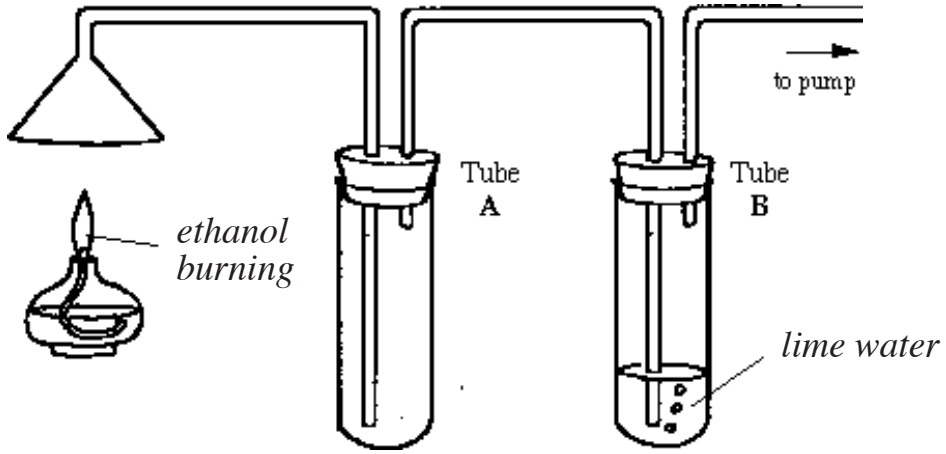


As well as sharing the same ***General formula***, the ***physical*** *properties* of the alkanols such as *melting point* (***increases***), *boiling point* (***increases***) and *solubility in water* (***decreases***) show a steady trend as the *molecular size* increases. For these reasons, the alkanols can be described as a ***homologous series***.

Property	***Result***
Appearance	***colourless liquids***
Solubility	***smaller alkanols are very soluble***
pH	***neutral, do not produce H^+ or OH^- ions in water***
Conduction	***covalent, so non-conductors***
Burning	***burn to produce CO_2 and H_2O***

Combustion of Ethanol

This activity is about the products of combustion reaction of ethanol



ethanol + ***oxygen*** → ***carbon dioxide*** + ***water***

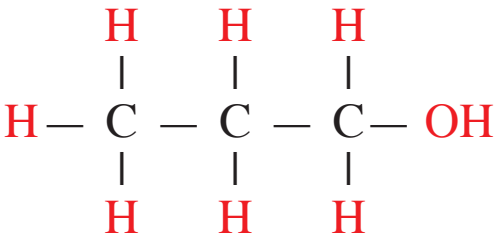
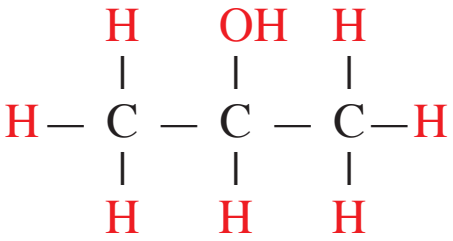
$$2\,C_2H_5OH + 5\,O_2 \rightarrow 4\,CO_2 + 6\,H_2O$$

The ***combustion*** of ethanol can be referred to as ***oxidation*** on the basis that the ***carbons*** and ***hydrogens*** are ' *gaining oxygen* '. Later in this topic *mild oxidation* of alcohols will lead to totally different, and much more important, products - ***aldehydes***, ***ketones*** and ***carboxylic acids***.

Straight-Chain Alkanols

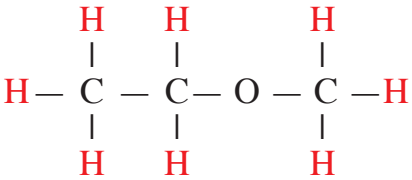
This activity considers how to use systematic names to indicate the position of the hydroxyl group in isomers

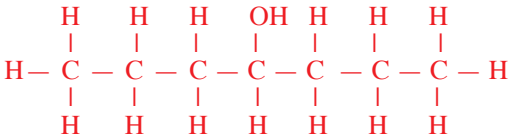
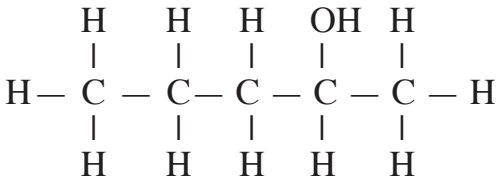
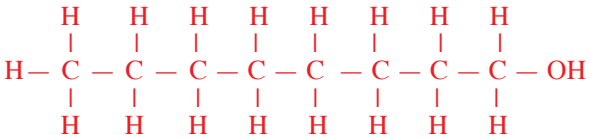
The position of the *hydroxyl* group can change to produce *isomers* without the need to introduce branches.

Full Structural		
Shortened Structural	$CH_3CH_2CH_2OH$	$CH_3CH(OH)CH_3$
Systematic Name	propan-1-ol	propan-2-ol

C_3H_6O

Isomers don't have to be from the same homologous series



Straight-Chain Alkanols	
Name:	heptan-4-ol
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2CH(OH)CH_2CH_2CH_3$
Name:	pentan-2-ol
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2CH(OH)CH_3$
Name:	octan-1-ol
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$

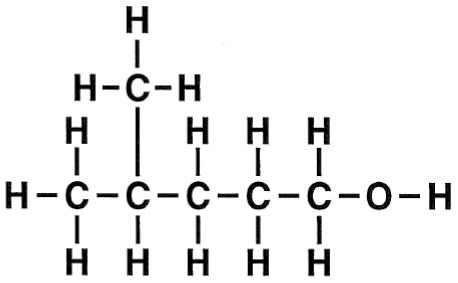
Branched-Chain Isomers

This activity considers how to use systematic names to indicate both the position of the hydroxyl group and the branch position in isomers of branched-chain alkanols

The 'longest chain' must include the functional group.

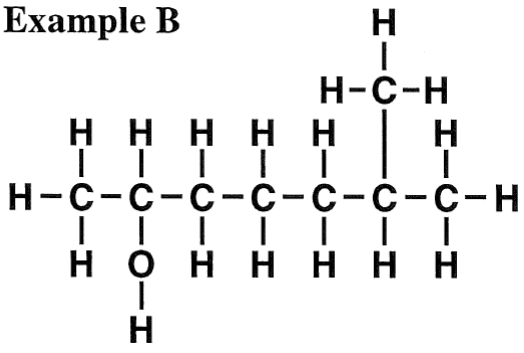
The chain is numbered from the end nearest the functional group

Example A

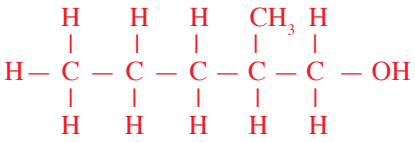
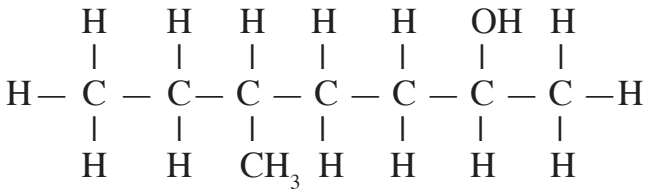
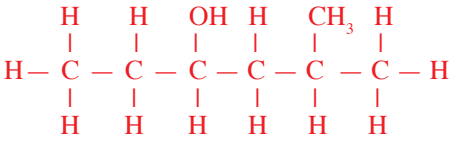
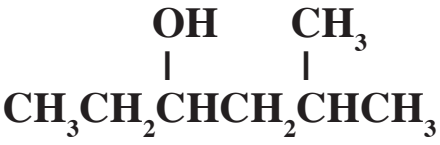


2-methylpentan-1-ol

Example B

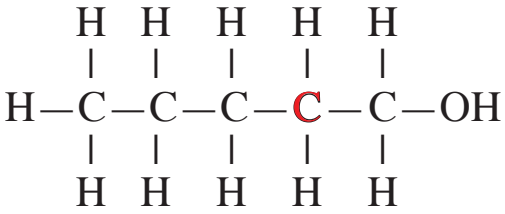


6-methylheptan-2-ol

Branched-Chain Alkanols	
Name:	2-methylpentan-1-ol
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2CH(CH_3)CH_2OH$
Name:	5-methylheptan-2-ol
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH(CH_3)CH_2CH_2CH(OH)CH_3$
Name:	4-methylhexan-3-ol
Full Structural Formula:	
Shortened Structural Formula:	

Primary, Secondary & Tertiary

This activity relates the classification of alcohols to their molecular structures

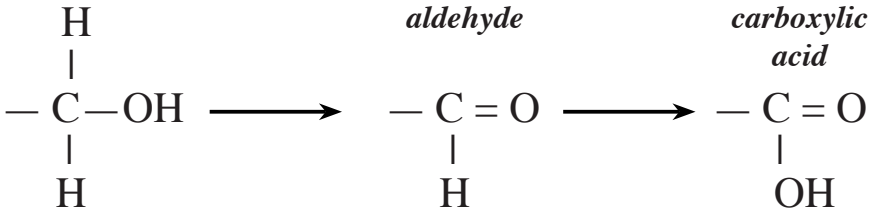


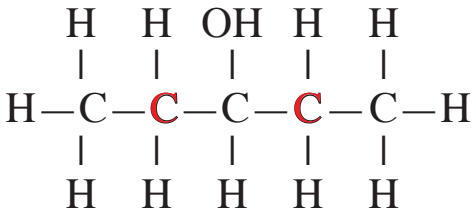
This is an example of a ***primary alcohol***.

It is so-called because only ***one carbon*** is directly attached to the carbon with the ***hydroxyl*** *group*.

The ***hydroxyl*** *group* is at the ***end of the chain***.

Systematic Name ***pentan-1-ol***

mild oxidation : ***primary alcohol***  ***aldehyde*** ***carboxylic acid***



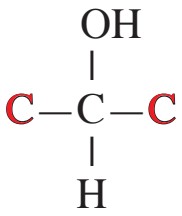
This is an example of a ***secondary alcohol***.

It is so-called because ***two carbons*** are directly attached to the carbon with the ***hydroxyl*** *group*.

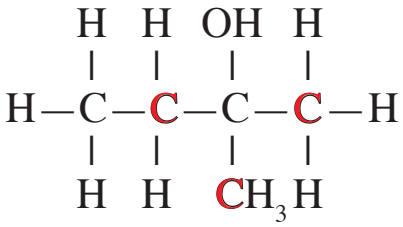
The ***hydroxyl*** *group* is ***along the chain***.

Systematic Name ***pentan-3-ol***

mild oxidation : ***secondary alcohol***



ketone



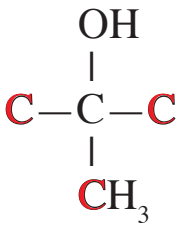
This is an example of a ***tertiary*** alcohol.

It is so-called because ***three carbons*** are directly attached to the carbon with the ***hydroxyl*** *group*.

The ***hydroxyl*** *group* is at ***a branched position*** of the chain.

Systematic Name ***2-methylbutan-2-ol***

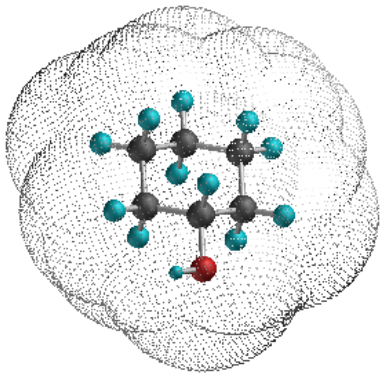
mild oxidation : ***tertiary alcohol***



no products from mild oxidation

Ring Structures

This activity looks briefly at the structures and names of the cyclalkanols



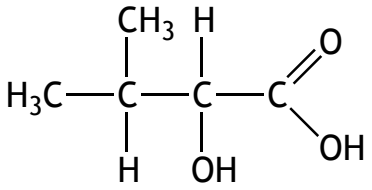
Molecular Formula	C_4H_7OH	C_5H_9OH
Full Structural		
Systematic Names		

Cycloalkanols are examples of ***secondary*** alcohols because there are ***two carbons*** attached to the carbon with the ***hydroxyl*** *group* - the hydroxyl group is 'along the chain'.

Cycloalkanols are ***not isomers*** of *alkanols*, because there are ***two less hydrogens*** in a ring structure compared to the equivalent chain structure.

Hydroxyl Group as Substituent

This activity demonstrates how the hydroxyl group is named in molecules with more important groups present.



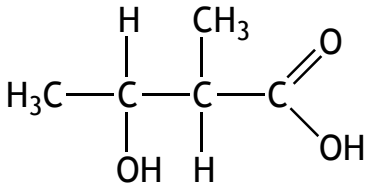
In this molecule the ***carboxylic*** acid group, —COOH, is ***more important*** and the presence of the —OH is signified by the use of the *prefix* '***hydroxy***' rather than the normal *suffix* '***-ol***'

2-hydroxy-3-methylbutanoic acid

Other groups that you might meet as suffixes:-

$—NH_2$ ***amine*** becomes ***amino***

—COOH ***carboxylic*** becomes ***carboxyl***



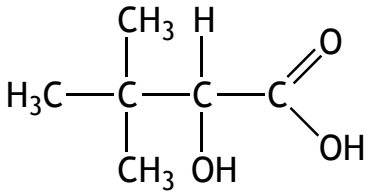
3-hydroxy-2-methylbutanoic acid

You are already familiar with:-

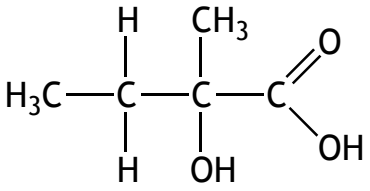
CH_4 ***methane*** becoming ***methyl***

But may also see:-

$—O—CH_3$ becoming ***methoxy***



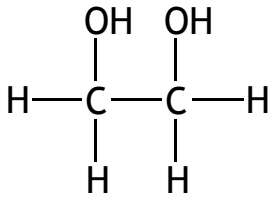
2-hydroxy-3,3-dimethylbutanoic acid



2-hydroxy-2-methylbutanoic acid

More Than One Hydroxyl Group

This activity looks at the structures and names of two alcohols which have more than one hydroxyl group

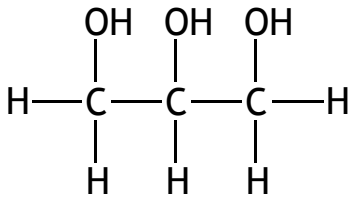


ethane-1,2-diol

The common name for this alcohol is ***glycol*** .

It is used as ***antifreeze*** in car ***radiators***.

It contains *two* ***hydroxyl*** *group* and can be referred to as a ***dihydric*** alcohol or a ***diol***.



propane-1,2,3-triol

The common name for this alcohol is ***glycol*** .

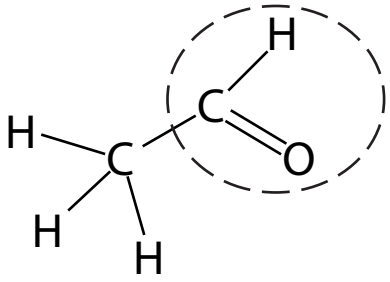
It has various culinary uses including ***ice-cream***

It contains *three* ***hydroxyl*** *group* and can be referred to as a ***trihydric*** alcohol or a ***triol***.

Aldehyde Structures

This activity considers the structures and systematic names of the alkanal series of aldehydes.

*An **alkanal** is a compound which contains the **carbonyl** group at the end position of a hydrocarbon chain in which all the carbon atoms are linked by single bonds.*

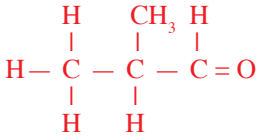
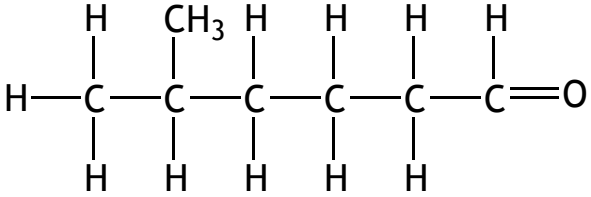
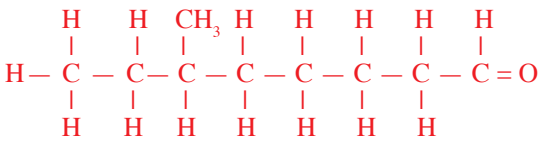


The ***functional*** *group* of an aldehyde contains the ***carbonyl*** *group* and a ***hydrogen*** atom - —CHO.

CH_3CHO

The longest carbon chain includes the ***functional*** *group*, so this molecule is named as ***ethanal***.

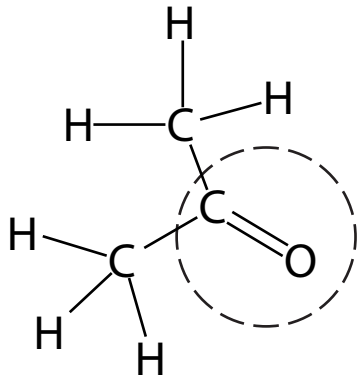
The chain is always numbered from the end with the —CHO functional group.

Alkanal Structures	
Name:	2-methylpropanal
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH(CH_3)CHO$
Name:	5-methylhexanal
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH(CH_3)CH_2CH_2CH_2CHO$
Name:	6-methyloctanal
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CHO$

Ketone Structures

This activity considers how to apply systematic names to the alkanone family of ketones.

*An **alkanone** is a compound which contains the **carbonyl** group at a position within a hydrocarbon chain where all the carbon atoms are linked by single bonds.*

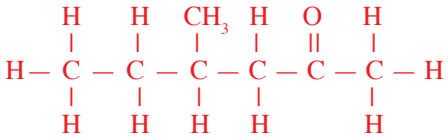
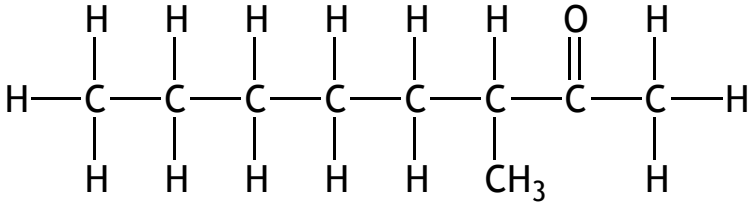
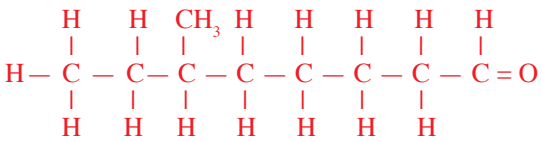


The ***functional*** *group* of a ketone is simply the ***carbonyl*** *group* by itself.

CH_3COCH_3

The longest carbon chain must include the ***functional*** *group*. This molecule is named as ***propanone***.

The chain is always numbered from the end nearest the —CO— functional group.

Alkanone Structures	
Name:	4-methylhexan-2-one
Full Structural Formula:	
Shortened Structural Formula:	$CH_3\,CH_2\,CH\,(CH_3)\,CH_2\,CO\,CH_3$
Name:	3-methyloctan-2-one
Full Structural Formula:	
Shortened Structural Formula:	$CH_3\,CH_2\,CH_2\,CH_2\,CH\,(CH_3)\,CO\,CH_3$
Name:	4-methylhexan-3-one
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CHCOCH_2CH_3$ (CH$_3$ branch on the CHCO carbon)

Alkanoic acids

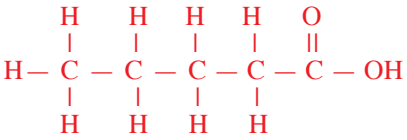
This activity considers the structures, formulae and systematic names of some of the members of the alkanoic acid family.

Any molecule that contains the *carboxyl group*, —COOH, can be considered as a *carboxylic acid*. The molecule could have a ***chain*** structure, a ***ring*** structure, it could be ***saturated*** (C—C) or ***unsaturated*** (C=C or C≡C).

*The **alkanoic acids** are compounds which contain the **carboxyl group** joined to a hydrocarbon **chain** in which all the carbon atoms are joined by **single** bonds.*

As usual, there are three ways to represent the formula of, for example, *pentanoic acid*

full structural formula



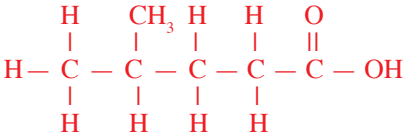
shortened structural formula

$CH_3CH_2CH_2CH_2COOH$

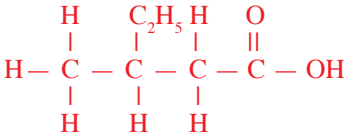
functional molecular formula

C_4H_9COOH

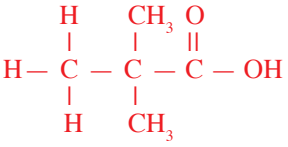
For naming purposes, the ***carbon*** of the ***carboxyl functional*** *group* is always taken as number 1, and the *'longest'* chain always starts with the ***functional*** *group*. For example:



4-methylpentanoic acid



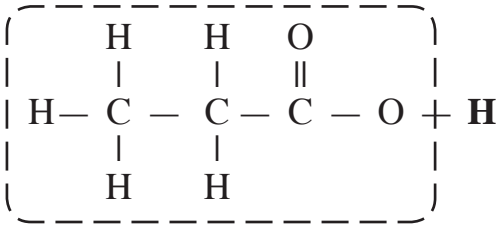
2-ethylbutanoic acid



2,2-dimethylpropanoic acid

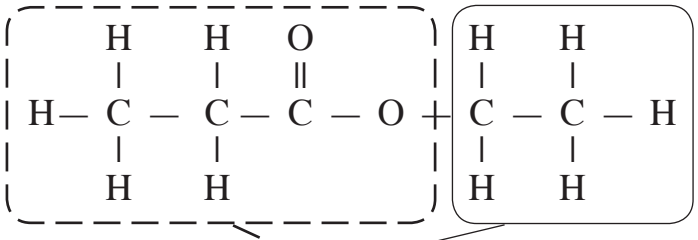
Simple Esters

This activity deals with naming and drawing full and structural formulae for esters.



The 'best'way to think about an ***ester*** is to consider it as an ***acid molecule*** which has had its ***hydrogen atom*** replaced by a ***carbon chain*** (an *alkyl group*).

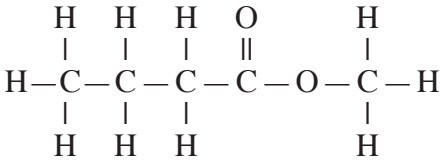
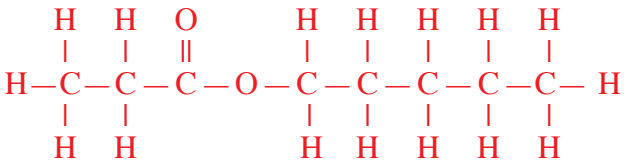
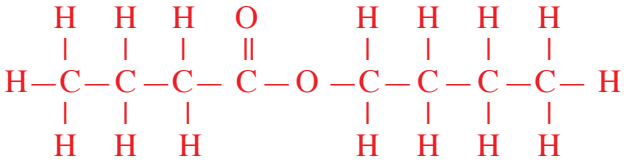
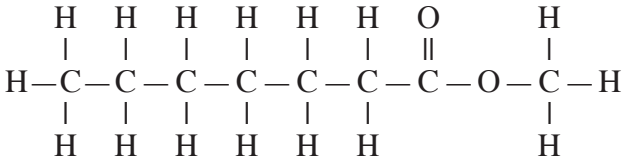
Learn to draw acids and you should find esters easy.

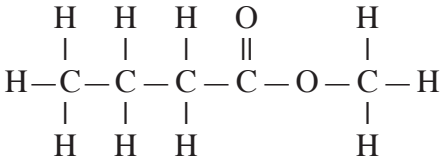
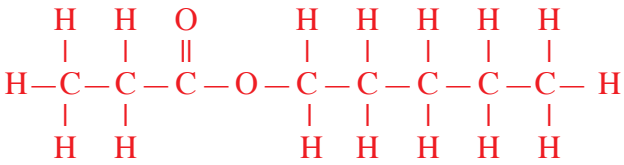
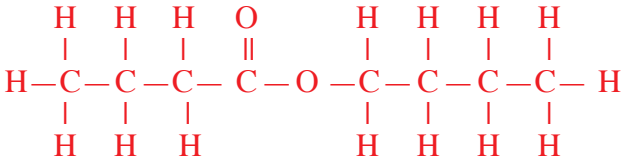
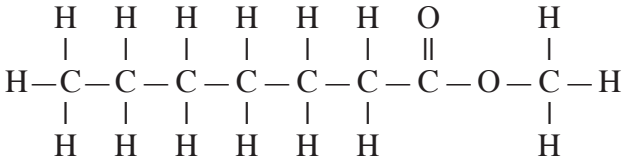


ethyl propanoate

As is often the case, we 'start' at the end of the name. *Identify the acid* (look for the ***carbonyl*** C = O) and give the ***ester*** its ***surname*** by changing the *—oic* ending to ***—oate***.

The *carbon chain* (derived from the parent ***alcohol***) is the ***'christian' name***, *—ol* changed to ***—yl***.

Ester Structures & Names	
Name:	***methyl butanoate***
Full Structural Formula:	
Shortened Structural Formula:	$\boldsymbol{CH_3CH_2CH_2COOCH_3}$
Name:	pentyl propanoate
Full Structural Formula:	
Shortened Structural Formula:	$\boldsymbol{CH_3CH_2COOCH_2CH_2CH_2CH_2CH_3}$
Name:	***butyl butanoate***
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$
Name:	***methyl heptanoate***
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2CH_2CH_2CH_2COOCH_3$

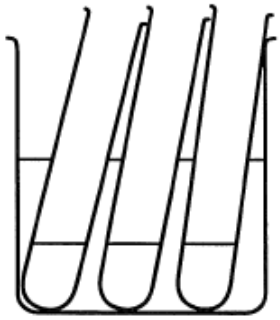
Ester Structures & Names	
Name:	***methyl butanoate***
Full Structural Formula:	
Shortened Structural Formula:	$\boldsymbol{CH_3CH_2CH_2COOCH_3}$
Name:	pentyl propanoate
Full Structural Formula:	
Shortened Structural Formula:	$\boldsymbol{CH_3CH_2COOCH_2CH_2CH_2CH_2CH_3}$
Name:	***butyl butanoate***
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$
Name:	***methyl heptanoate***
Full Structural Formula:	
Shortened Structural Formula:	$CH_3CH_2CH_2CH_2CH_2CH_2COOCH_3$

5.3 Oxidation Reactions

This topic examines how the different types of alcohol are oxidised and the different types of product produced.

Comparing Oxidation

This activity compares the oxidation reactions of the three types of alcohol



Acidified *potassium* ***dichromate*** is a mild *oxidising agent* that *changes* ***colour*** when it reacts.

$$\underset{\text{orange}}{Cr_2O_7^{2-}} + 14\,H^+ + 6\,e^- \longrightarrow \underset{\text{green}}{2\,Cr^{3+}} + 7\,H_2O$$

A large number of H^+ ions are consumed, hence the need to use an ***acidified*** solution or reaction would be too ***slow***.

Three different *types* of alcohol were added to some *dichromate* solution and placed in a hot ***water*** *bath* for a few minutes.

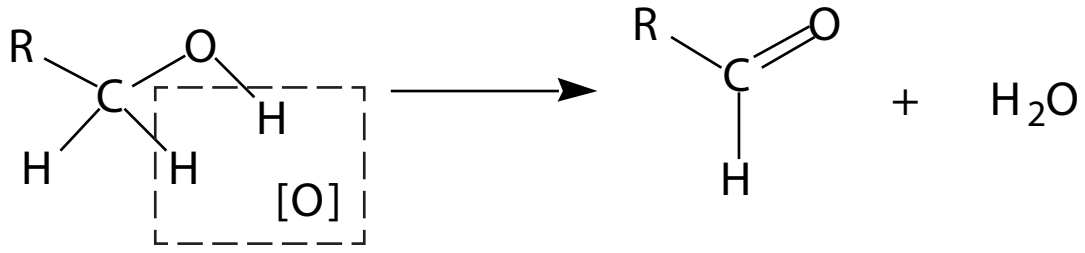
Name of alcohol	*Type of alcohol*	*Colour change observed*
butan-1-ol	***primary***	***orange*** → ***green***
butan-2-ol	***secondary***	***orange*** → ***green***
2-methylpropan-2-ol	***tertiary***	***orange*** → ***orange***

Both Primary and Secondary alcohols can be oxidised but Tertiary alcohols cannot.

The Oxidation Reaction

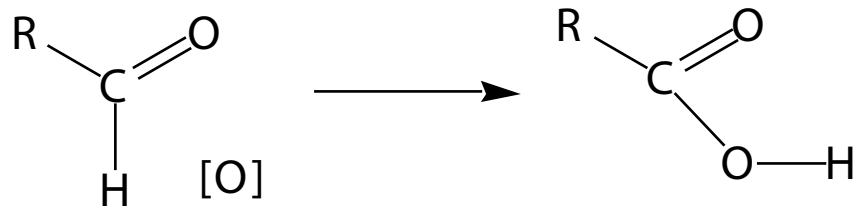
This activity explains the changes which occur when different types of alcohol are oxidised.

Primary *alcohols* can be ***oxidised*** in two stages. The *oxidising agent* is simply the source of ***oxygen*** [O].



During the first stage the ***hydroxyl*** *group* C—OH is converted into a ***carbonyl*** *group*, C=O. The molecule produced is called an ***aldehyde***.

The second stage sees the ***aldehyde*** converted into an ***acid*** .



Notice that ***oxidation*** can involve the ***loss of hydrogens*** as well as the ***gain of oxygen*** (and, of course, oxidation is still the ***loss of electrons***).

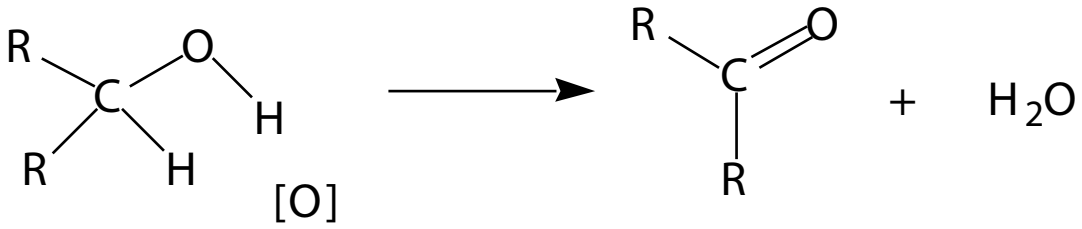
In Organic Chemistry it is often more convenient to use the following definitions:

OXIDATION - an ***increase*** in the ***oxygen:hydrogen*** ratio (***gain*** O or ***lose*** H)

REDUCTION - a ***decrease*** in the ***oxygen:hydrogen*** ratio (***lose*** O or ***gain*** H)

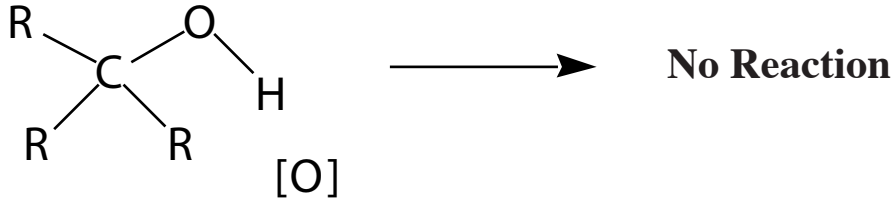
Name	*Molecular Formula*	*Number of O atoms*	*Number of H atoms*	*Oxygen: Hydrogen ratio*
ethanol	C_2H_6O	*1*	*6*	*1 : 6*
ethanal	C_2H_4O	*1*	*4*	*1 : 4*
ethanoic acid	$C_2H_4O_2$	*2*	*4*	*1 : 2*

Secondary *alcohols* can also be ***oxidised*** , but they can only go through the first stage. Again,the *oxidising agent* is simply the source of ***oxygen*** [O].



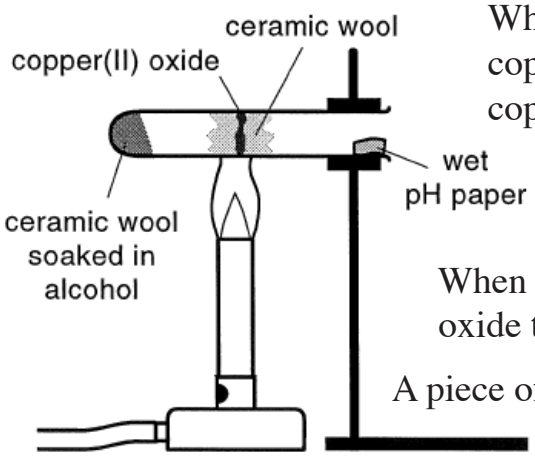
Again, during the first stage of oxidation the ***hydroxyl*** *group* C—OH is converted into a ***carbonyl*** *group*, C=O. The molecule produced this time is called a ***ketone*** . The absence of a ***hydrogen*** atom makes it impossible for this molecule to be ***oxidised*** a *second* time to form an ***acid***.

Tertiary *alcohols* cannot be ***oxidised*** . The absence of ***hydrogen*** atoms makes *oxidation* impossible.



Oxidising With Copper (II) Oxide

This activity investigates another method for oxidising primary and secondary alcohols



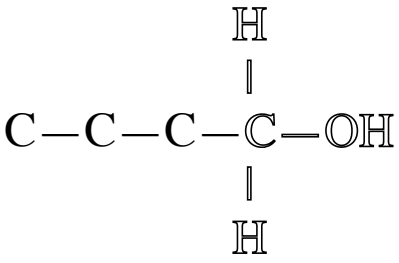
When a ***primary*** *alcohol* is passed over heated copper (II) oxide the ***black*** oxide turns into ***reddy-brown*** copper metal.

A piece of ***pH paper*** held at the mouth of the test-tube turns ***red*** - an ***acid*** has been formed.

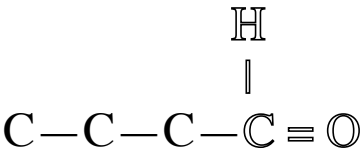
When a ***secondary*** *alcohol* is passed over heated copper (II) oxide the ***black*** oxide turns into ***reddy-brown*** copper metal.

A piece of ***pH paper*** held at the mouth of the test-tube stays the same because an ***acid*** has ***not*** been formed.

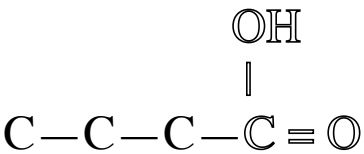
Summary



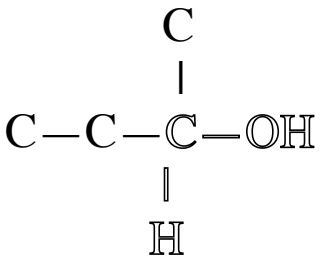
a ***primary*** *alkanol*
(—OH at end of chain)
butan-1-ol



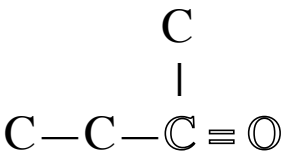
an *alkanal*
(C=O at end of chain)
butanal



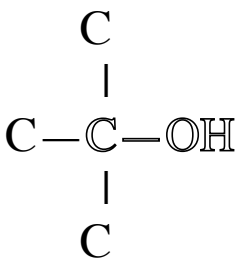
an *alkanoic acid*
(COOH at end of chain)
butanoic acid



a ***secondary*** *alkanol*
(—OH in middle of chain)
butan-2-ol



a *alkanone*
(C=O in middle of chain)
butanone



a ***tertiary*** *alkanol*
(—OH at same place as a branch)
2,methylpropan-2-ol

Oxidation of Aldehydes

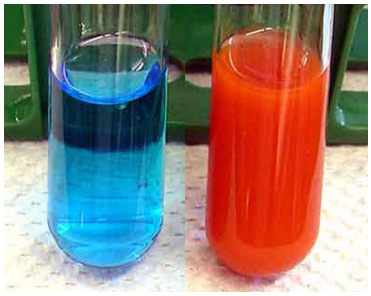
This activity investigates other oxidising agents that can be used to distinguish aldehydes from ketones

Acidified *potassium* ***dichromate*** is a mild *oxidising agent* that *changes* ***colour*** when it reacts.

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

orange → *green*

A large number of H^+ ions are consumed, hence the need to use an ***acidified*** solution or reaction would be too ***slow***.



Fehling's or ***Benedict's*** are another two mild *oxidising agents* that *change* ***colour*** when they react.

$$Cu^{2+} + e^- \longrightarrow Cu^+$$

blue solution → *red-brown solid*

Tollen's solution is another mild *oxidising agent* that *changes* ***state*** when it reacts.

$$Ag^+ + e^- \longrightarrow Ag$$

colourless solution → *silvery solid*

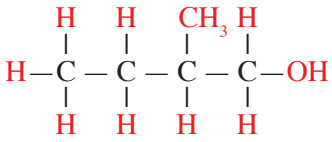
Sometimes the silver attaches to the surface to give a '***silver mirror***' effect.

Tollen's and ***Fehling's*** solutions can only be used to ***oxidise aldehydes***. They do ***not*** usually react with ***primary*** or ***secondary*** alcohols. This makes ***acidified dichromate*** the only '*universal*' ***oxidising agent***.

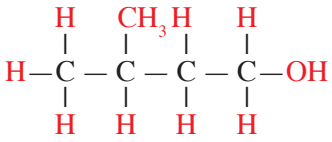
Food Chemistry 1

The aim of this activity is to introduce some of the oxygen containing compounds that have important roles as flavour molecules and the problems that oxidation can bring.

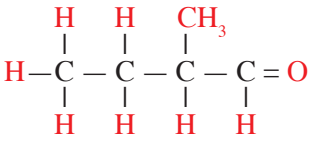
Though there are many ***molecules*** responsible for the valued ***smell*** of *truffles*, two ***alcohols*** and two ***aldehydes*** are found in the highest ***concentrations***. ***Alcohols*** and ***aldehydes*** such as these are easily ***oxidised***. When that happens, the truffles lose their characteristic ***aroma*** and ***flavour***.



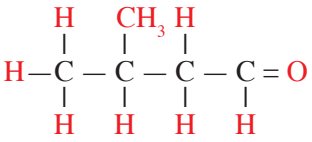
2-methylbutanol



3-methylbutanol

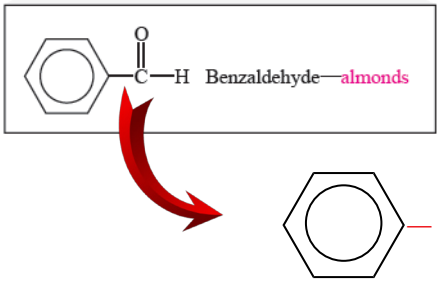


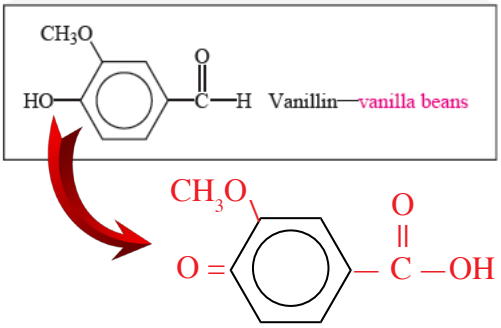
2-methylbutanal

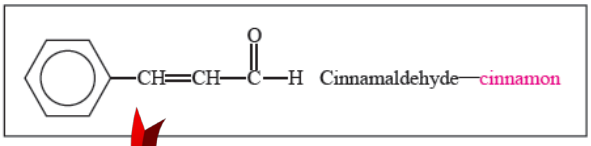


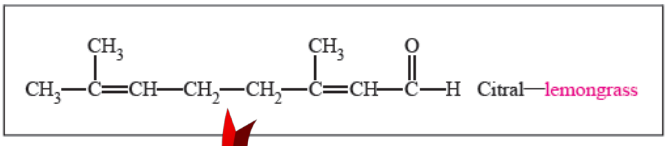
3-methylbutanal

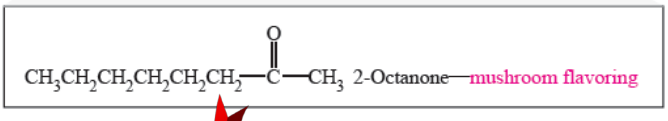
Most flavour molecules are more complex, but many contain the ***alcohol***, ***aldehyde*** or ***ketone*** functional groups.Thay can be, however, vulnerable to ***oxidation*** which will almost certainly change the nature of their ***flavour***.While small acids such as ***methanoic*** and ***ethanoic*** *acid* are '*vinegary*', others such as ***propanoic*** and ***butanoic*** *acid* are '*cheesey*' and '*sickly*' and can be responsible for the *rancid* smells of food '*going off*'









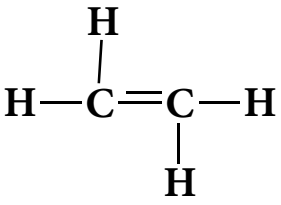


No ***oxidation*** product as this only contains the ***ketone*** group

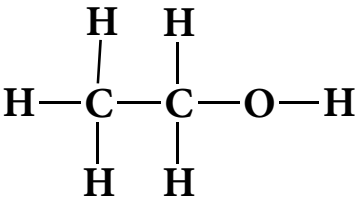
Free Radicals

The aim of this activity is to introduce free radicals.

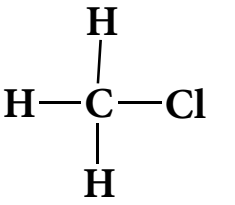
Organic chemistry largely involves ***stable covalent*** *molecules* with ***covalent*** *bonds* - a ***pair*** of ***electrons*** *shared between* two atoms.



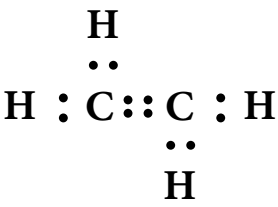
ethene

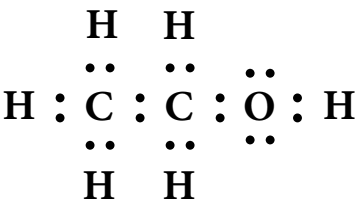


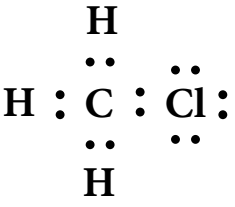
ethanol



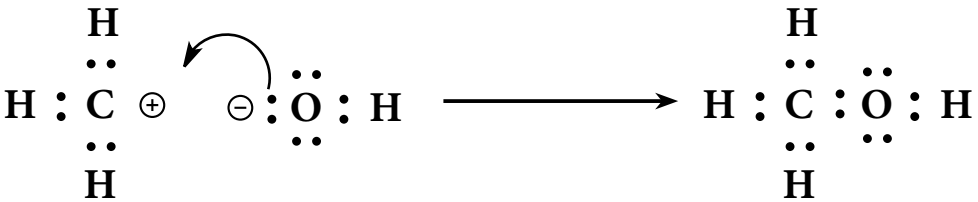
chloromethane

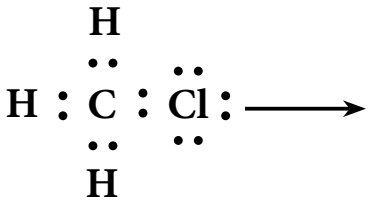


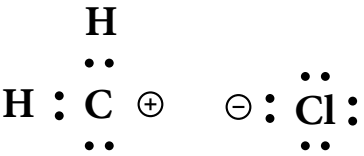




Often, reactions involve the ***breaking*** of ***polar*** bonds to form ***temporary***, very ***reactive*** ions (***the activated complex***) and ***electrons*** tend to remain as ***pairs of electrons***. ***Ions*** with **4** ***pairs of electrons*** - *the stable octet* - ***will not need to react further***.







This is an example of a ***substitution*** reaction as a ***chlorine*** atom is ***removed*** to be ***replaced*** by the ***hydroxyl*** group

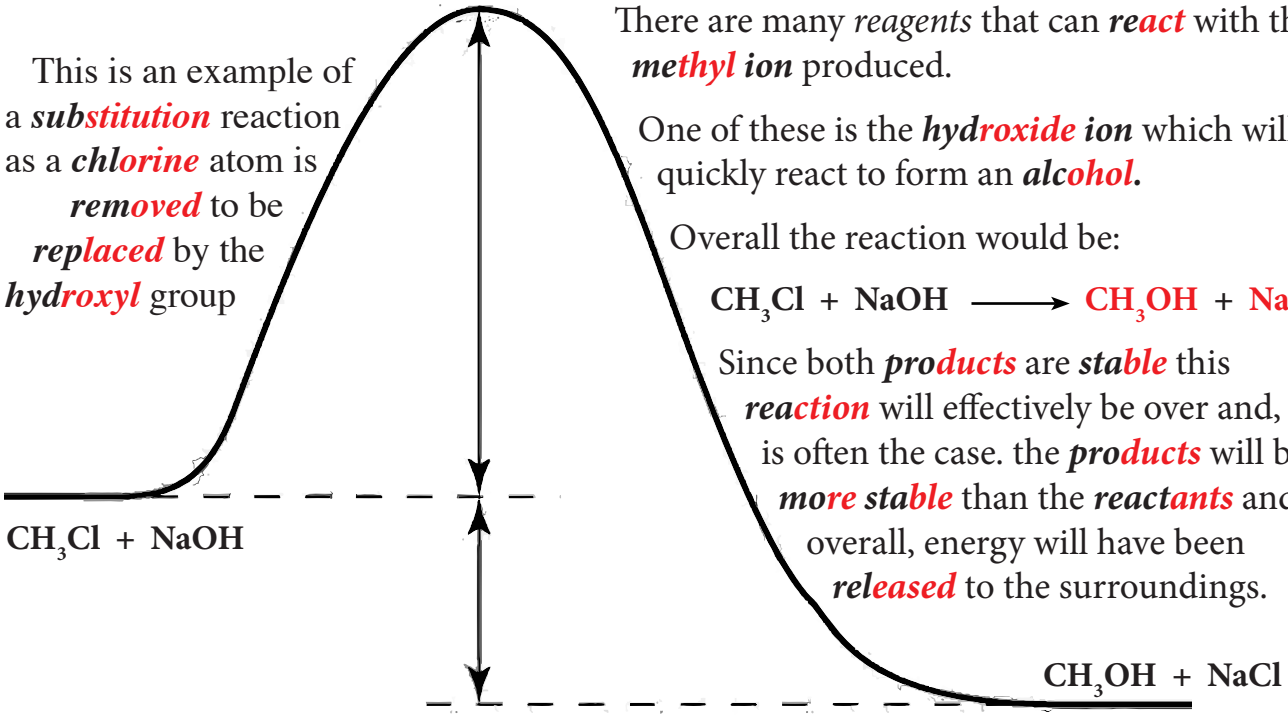
There are many *reagents* that can ***react*** with the ***methyl ion*** produced.

One of these is the ***hydroxide ion*** which will quickly react to form an ***alcohol.***

Overall the reaction would be:

$CH_3Cl + NaOH \longrightarrow CH_3OH + NaCl$

Since both ***products*** are ***stable*** this ***reaction*** will effectively be over and, as is often the case. the ***products*** will be ***more stable*** than the ***reactants*** and, overall, energy will have been ***released*** to the surroundings.



Whilst ***polar bonds*** are generally easier to break, ***non-polar bonds*** can also break, though extra ***energy***, in the form of ***light***, is often required. When these bonds ***break***, each atom retains its own electron but ***very unstable***, ***very reactive free radicals*** are formed.

When ***light*** of the correct ***energy*** strikes a ***bond***, the ***energy*** can be ***absorbed***.

$$Cl - Cl \longrightarrow 2\,Cl\bullet$$

In ***chlorine molecules***, Cl_2 , each ***chlorine atom*** is surrounded by 4 ***electron pairs*** and they are ***stable***. When the bond ***breaks***, each ***chlorine*** atom has only 3 ***electron pairs***. There are still ***equal numbers*** of ***protons*** (***17***) and ***electrons*** (***17***) present so these are ***atoms*** *not* ***ions***.

Similarly, the ***non-polar*** O — O ***bond*** in ***hydrogen peroxide*** can easily break to produce ***free radicals***:-

$$H - O - O - H \longrightarrow 2\ \bullet OH$$

Free Radical Chain Reaction

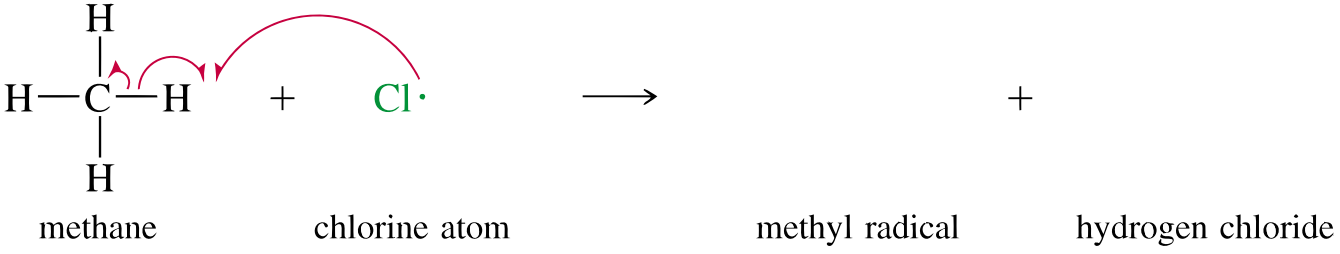
The aim of this activity is to examine how reactions involving free radicals lead to a chain reaction .

When a ***free radical*** reacts with another ***molecule***, a *new* ***free radical*** is *always* produced. This new ***free radical*** can then go on and react to ***produce another*** *free radical* and so the ***reaction continues*** '*forever*' - a ***chain reaction***.

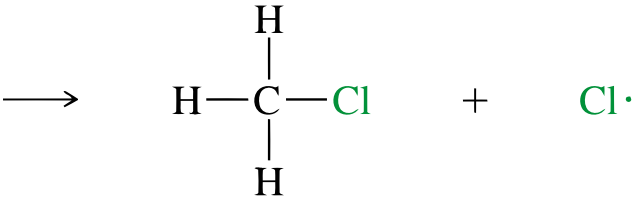
For example, the ***substitution*** reaction between and ***alkane*** and a ***halogen*** has a number of steps which will repeat '*forever*'.

Initiation: *needed to produce a free radical to start each chain.*

Propagation: *the steps that will see a free radical react but a new free radical produced to keep the chain reaction going.*

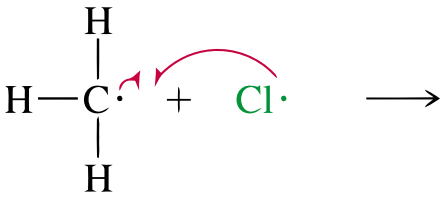


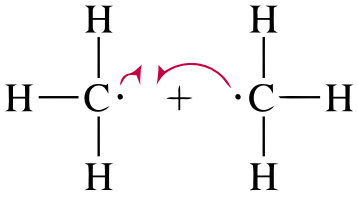
Second propagation step

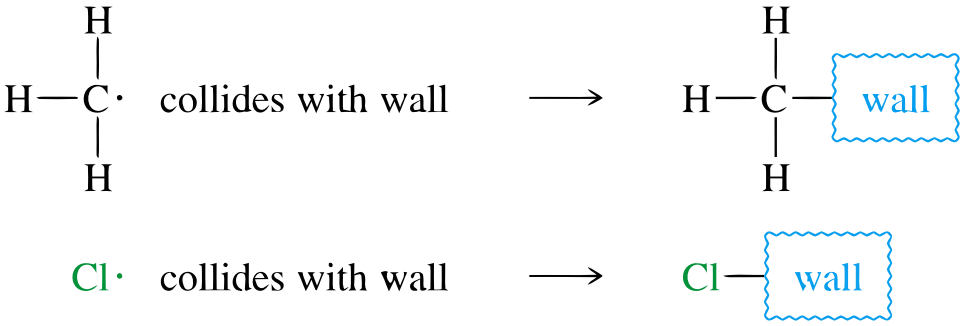


methyl radical chlorine molecule chloromethane chlorine atom

Termination: *the steps that will see a chain eventually stopped*







Detailed descriptions of the ***steps*** involved in a reaction - showing the ***movement*** of ***electrons*** as bonds ***break*** and ***form*** - is called a ***Reaction Mechanism***.

Overall the reaction is simply:

$$CH_4 + Cl_2 \longrightarrow \mathbf{CH_3Cl} + \mathbf{HCl}$$

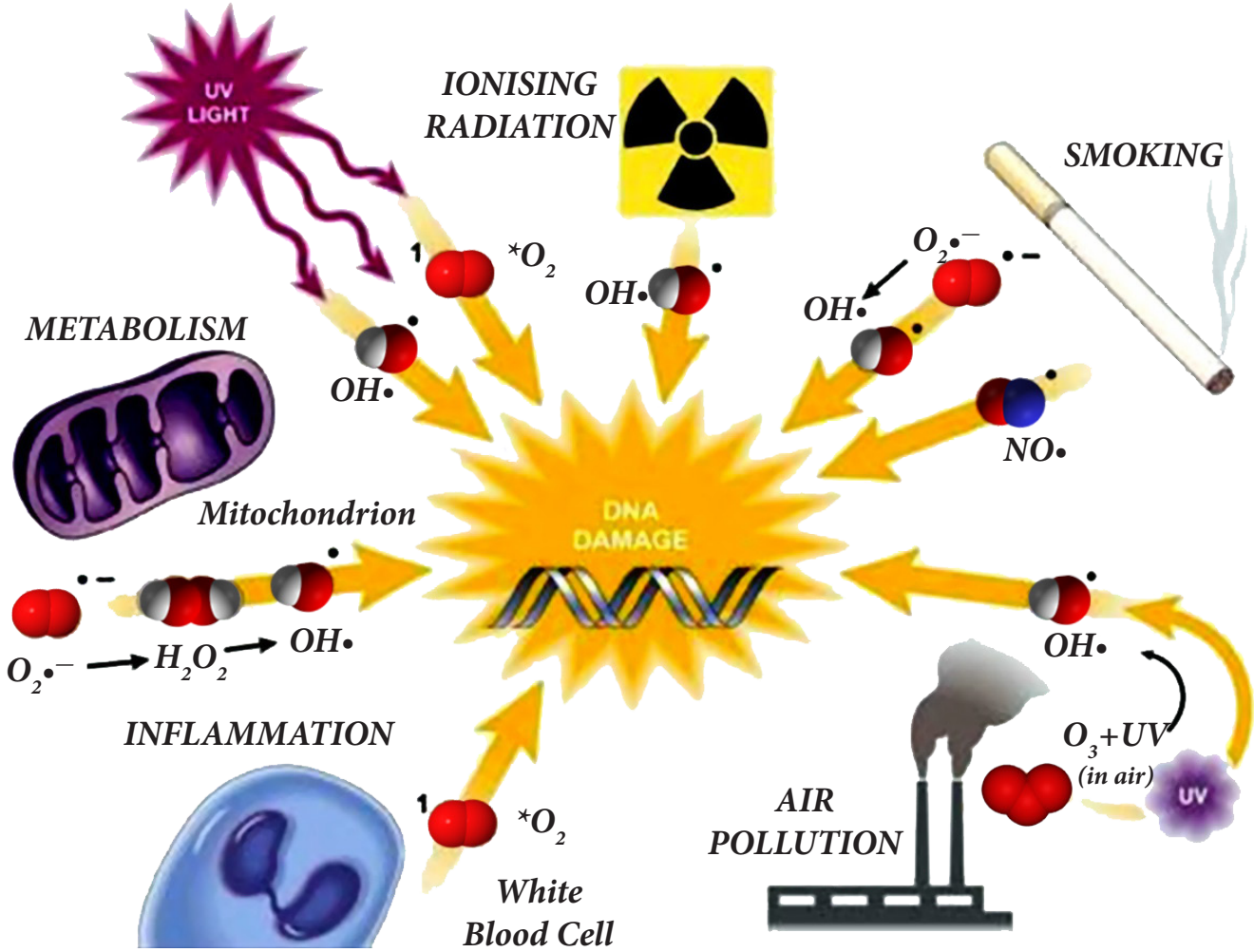
This is another example of a ***Substitution*** reaction and is the characteristic reaction of ***saturated*** hydrocarbons such as ***alkanes***. The reaction with ***bromine*** *vapour* or ***bromine*** *water* is often used as the test for ***saturation***. Both ***saturated*** and ***unsaturated*** molecules can ***decolourise*** bromine, but *at very different rates*,

$C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$ ***slow***, ***substitution***, in *light*

$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$ ***fast***, ***addition***, even in *dark*

Free Radical Oxidation

The aim of this activity is to examine how free radical oxidation leads to problems with food shelf-life as well as natural ageing in organisms.

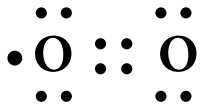


The ***radicals*** of most concern in ***biological*** *systems* are derived from ***oxygen*** and are known collectively as *reactive oxygen species* or ***RAS***. The main 3 are opposite:

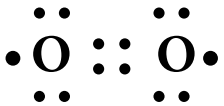
Whilst some ***radicals*** are formed by ***external*** processes, many are formed as necessary ***intermediates*** in a variety of normal ***biochemical*** reactions.

However, when generated in excess or not appropriately controlled (by natural ***antioxidants***), radicals can wreak havoc on a broad range of ***macromolecules*** such as ***lipids*** (*fats & oils*), ***phospholipids*** (*cell membranes*) and ***proteins*** including parts of DNA and RNA.

superoxide $O_2•^-$

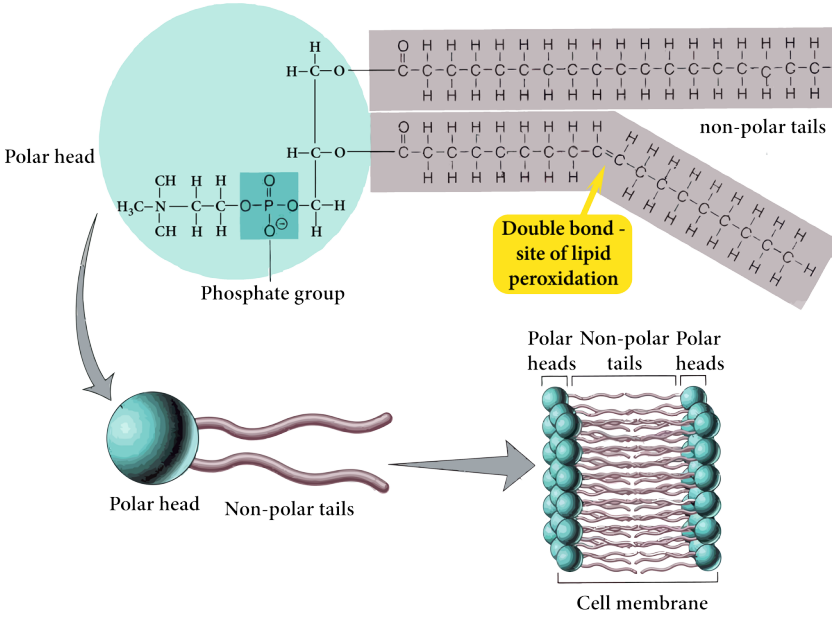


peroxide $O_2•^{2-}$



hydroxyl **OH•**

Macromolecules such as ***lipids*** (derived from *fatty acids*), ***proteins*** and ***nucleic*** acids (DNA) are particularly vulnerable to damage through a process known as ***lipid peroxidation***.



The reaction between ***oxygen*** based ***radicals*** and the C = C ***double*** bond can often progress from:

—OH ***hydroxyl***

to

—C = O ***carbonyl***

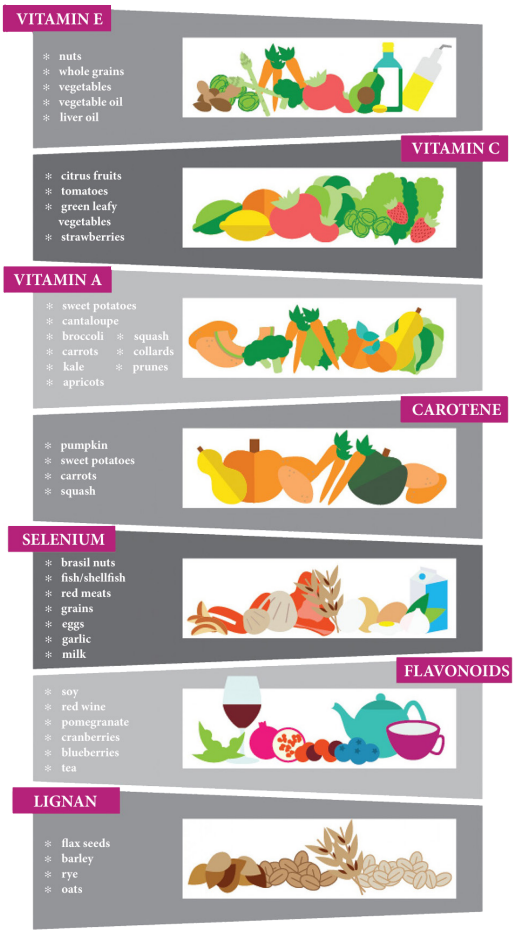
to

—COOH ***carboxyl***

and the carbon ***chain*** will often ***break*** at the site of the original C = C bond.

Antioxidants

The aim of this activity is to examine some antioxidants and the types of food in which they can be found.



If fats ***oxidise***, they can produce "off" ***odours*** and ***flavours*** (*stale, rancid odours*). Many of the molecules produced are ***aldehydes***, ***ketones*** or ***carboxylic acids***.

Many ***vitamins*** also oxidise and lose their activity.

If food ***pigments*** oxidise, they can change ***colour*** completely. For example, *red* meat turns *gray* when the *myoglobin* ***pigment oxidises***. In this case, the product is not unsafe; it just looks less appealing.

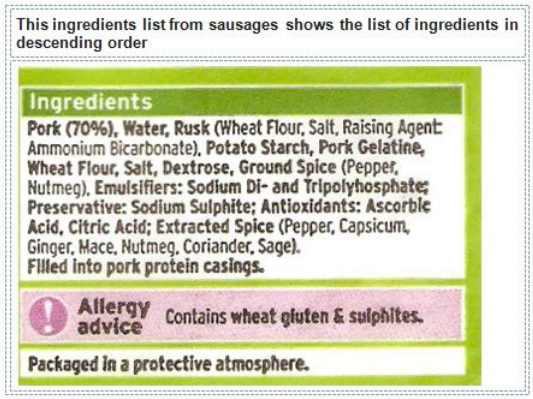
Antioxidants can be classified as one of two types:

'*traditional*' ***reducing agents*** or

free radical scavengers

Wine makers, for example, use SO_2 and/or ***sulphites*** (SO_2 » SO_3^{2-} in water) to slow down or prevent oxidation. Sausages and other processed meats similarly use ***sulphites*** or ***nitrites*** as ***preservatives***.

Similarly, ***Vitamin C*** (*ascorbic acid*) is a *natural* ***antioxidant*** found in many foods.



Half-equations for the ***oxidation*** reactions that these ***reducing agents*** (*antioxidants*) undergo can be written:

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2H^+ + 2e^-$$

Similarly for ***Vitamin C***:

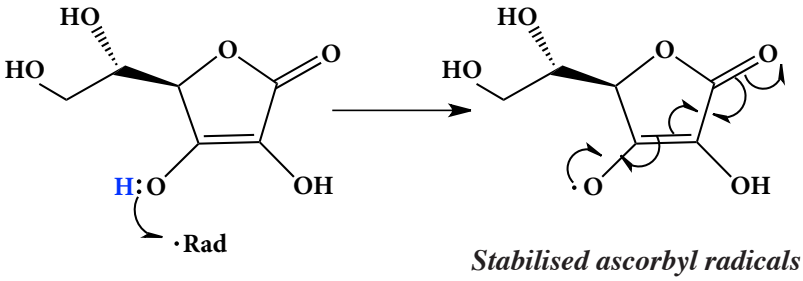
$$C_6H_8O_6 \longrightarrow C_6H_8O_6 + 2H^+ + 2e^-$$

Many of our ***antioxidants*** are also ***free radical scavengers*** which

can ***react with free radicals***

but ***form stable molecules***

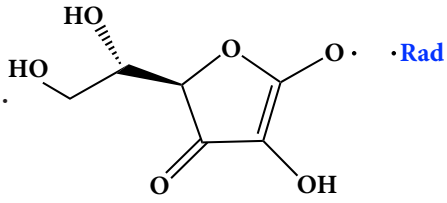
and ***prevent chain reactions***



Stabilised ascorbyl radicals

By ***moving*** the ***single electron*** around the molecule, it is possible to form a ***stable radical*** and ***stop the chain reaction***.

In addition, this molecule can go on and '*mop up*' a ***second radical*** making them even more effective.



Free Radical Scavengers

The aim of this activity is to examine some other applications of Free Radical Scavengers

It is not just ***food*** that we need to protect from ***oxidation***, particularly ***free radical oxidation*** brought about by exposure to ***UV radiation*** present in ***sunlight***.

Sun Blocks: whilst they contain white ***pigments***, such as *titanium oxide*, which try and ***block*** the ***UV light***, they also contain ***free radical scavengers*** to help ***minimise*** the ***damage*** caused by ***free radicals*** - such as ***aging*** of the ***skin***.

Cosmetics: for similar reasons, many ***cosmetics*** now include ***free radical scavengers*** among their ***ingredients***.

Plastics: many ***plastics*** contain *groups* that are *vulnerable* to ***free radical oxidation*** so ***free radical scavengers*** are added to prolong their use.

However, other plastics deliberately incorporate ***UV absorbing groups*** to ***accelerate*** the *breakdown* of the ***plastic*** and make it more *biodegradeable*.