Edexcel

AS - Level

Chemistry

CODE: (WCH11)

Topic 5

Alkanes

5A – 1 Alkenes and their bonding

WHAT ARE ALKENES?

You have already discovered a lot of information about alkanes, but so far you have only come across alkenes as examples used to illustrate nomenclature and isomerism.

The main difference between alkanes and alkenes is that alkanes contain only single bonds, but alkenes contain at least one C=C double bond, so they are unsaturated. Alkenes are much less common than alkanes, but they can be made from alkanes in cracking reactions.

GENERAL FORMULA FOR ALKENES

The structures and names of some common alkenes are shown in table A

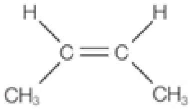
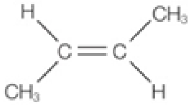
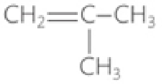
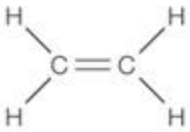
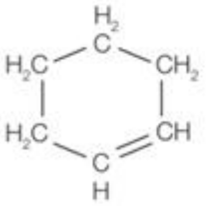
STRUCTURE	NAME
$CH_2{=}CH_2$	ethene
$CH_2{=}CH{-}CH_3$	propene
$CH_2{=}CH{-}CH_2{-}CH_3$	but-1-ene
	cis-but-2-ene
	trans-but-2-ene
 $CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{-}CH_3$	methylpropene

table A The structures and names of some common alkenes.

When drawing the structures of alkenes, you normally show the bonds at angles of 120°. For example, ethene would be shown as:



Just as some alkanes are cyclic, so are some alkenes. A common cyclic alkene is cyclohexene. The structure of cyclohexene is:



WHAT IS A C=C DOUBLE BOND?

In some ways, the use of the symbol C=C to represent a double bond is very useful, for example, it makes writing the structures of alkenes straightforward. However, it can be somewhat misleading, because it implies that the two bonds between the carbon atoms are the same. They are not.

In an alkene molecule, both carbon atoms in the C=C double bond are joined to only three other atoms (in alkanes, it is four other atoms). You may remember from Topics 2A.3 and 3C.1 that:

- electrons can exist in s orbitals and p orbitals
- pairs of electrons around an atom can be represented by a balloon shape.

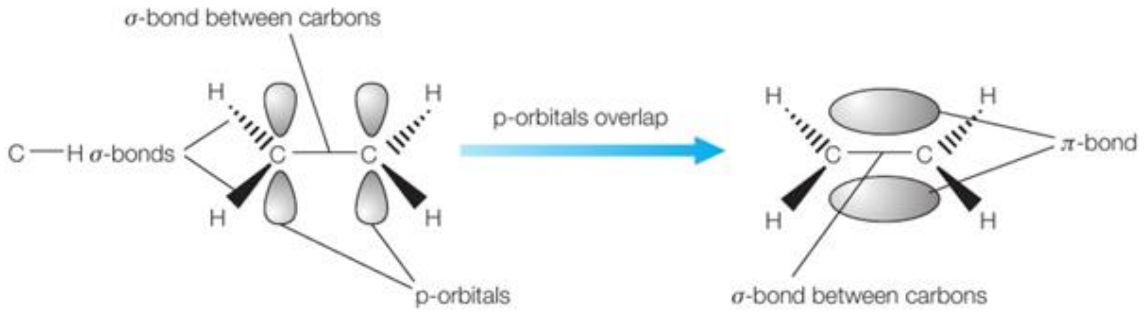
SIGMA BONDS

All of the single covalent bonds you have met so far involve the merging or overlapping of the orbitals of two different atoms.

They may involve the overlapping of two s orbitals, or one s orbital and one p orbital, or two p orbitals. All of these bonds are represented by a straight line. The covalent bond between the two hydrogen atoms in a hydrogen molecule can be shown as H-H. All of these types of bond can be referred to as sigma bonds (σ-bonds).

PI BONDS

When they do overlap, this results in the formation of two regions of negative charge above and below the C-C sigma bond. This type of bond is formed by the sideways overlap of orbitals, and bonds of this type are referred to as pi bonds (π-bonds).



SUBJECT VOCABULARY

sigma bonds covalent bonds formed when electron orbitals overlap axially (end-on)
pi bonds covalent bonds formed when electron orbitals overlap sideways

5A – 2 Geometric isomerism

STEREOISOMERISM

You learned about structural isomerism in Topic 4A.5. Structural isomers are compounds with the same molecular formula but with different structural formulae. Now we are going to consider a different type of isomerism called stereoisomerism. This is the overall term for two types of isomerism that you need to know about.

One type of stereoisomerism is optical isomerism, which you will meet in Topic 15. The other type is geometric isomerism, which we will look at in this topic.
All the types of isomerism you will meet in this course are shown in fig A in the form of a family tree.

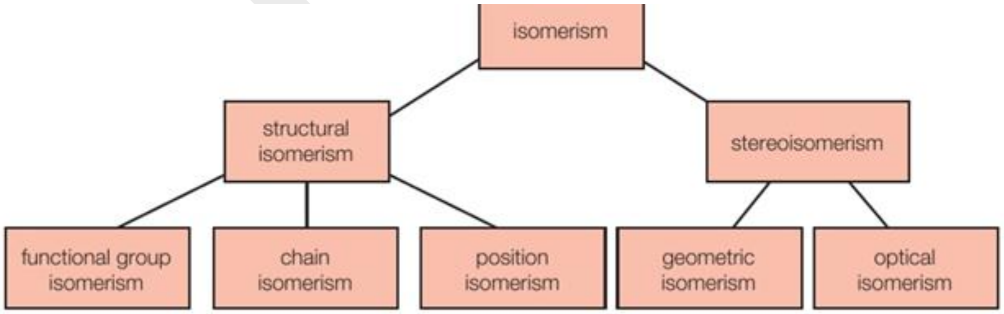


fig A The isomerism family tree.

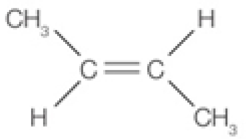
GEOMETRIC ISOMERISM

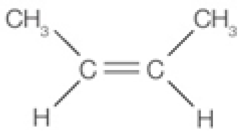
Geometric isomers differ from each other because their atoms or groups are attached at different positions on opposite sides of a C=C double bond.

To understand this, start by considering the alkene but-2-ene. Its structural formula can be shown as:

$CH_3—CH=CH—CH_3$

Unfortunately, showing the structure like this (with the atoms in a straight line) does not help us understand what geometric isomerism is. We need to show the bonds at angles of 120° to each other. Now you can see that there can be two different arrangements:





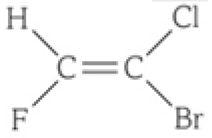
The left-hand structure shows the two CH3 groups further apart from each other. They are across the molecule. We add the abbreviation trans- (Latin for 'across') to the beginning of the name to indicate this. Think of the word transatlantic, which means at opposite ends of the Atlantic Ocean. The complete name is trans-but-2-ene.

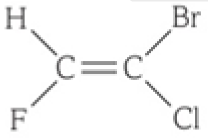
These two compounds are known as **geometric isomers**. This type of stereoisomerism is described as cis-trans isomerism or geometric isomerism.

This type of isomerism can exist in alkenes but not in alkanes. This is because there needs to be a C=C double bond for cis- and trans-isomers to occur. The presence of a C=C double bond leads to restricted rotation, so that there cannot be any rotation around the double bond. The groups attached to each C in C=C can only be in one of two positions.

E-Z NAMING SYSTEM

There is a problem with the cis-trans naming system. It only works with some compounds. Consider these two examples:

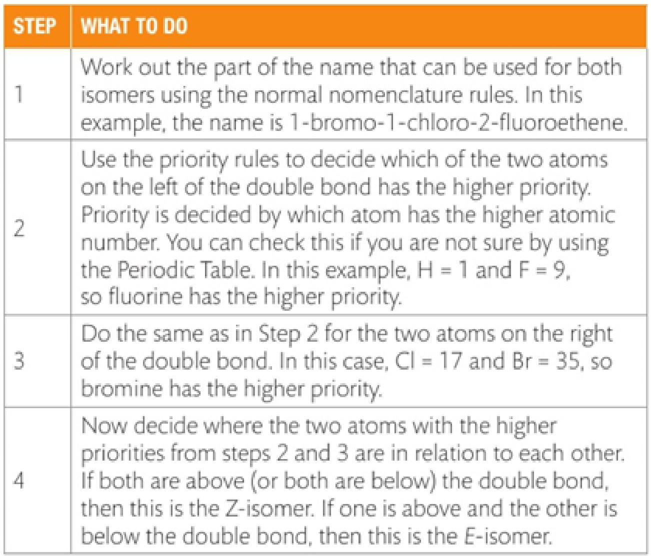




Because there are four different atoms attached to the C=C, the idea of two identical groups (or atoms in this example) being in a cis- or trans-arrangement cannot work.

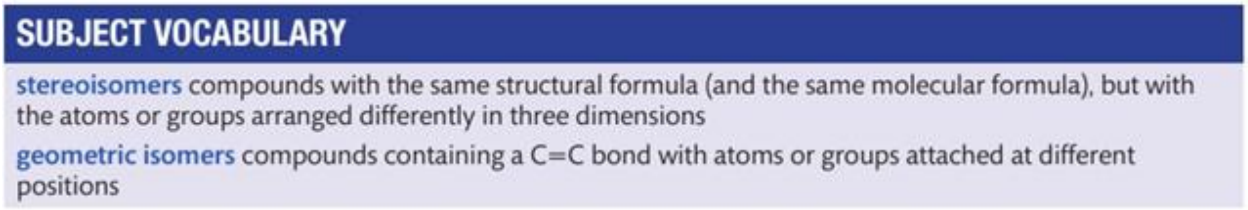
WHERE DO E AND Z COME FROM?

There are several ways to remember the difference between E and Z, and you might be able to work out a memorable way yourself. For now, try thinking about enemies, a word that begins with E. Enemies are far apart. You don't need a separate way to remember Z, as the Z-isomer is the one that isn't the E-isomer.



STEP	WHAT TO DO
1	Work out the part of the name that can be used for both isomers using the normal nomenclature rules. In this example, the name is 1-bromo-1-chloro-2-fluoroethene.
2	Use the priority rules to decide which of the two atoms on the left of the double bond has the higher priority. Priority is decided by which atom has the higher atomic number. You can check this if you are not sure by using the Periodic Table. In this example, H = 1 and F = 9, so fluorine has the higher priority.
3	Do the same as in Step 2 for the two atoms on the right of the double bond. In this case, Cl = 17 and Br = 35, so bromine has the higher priority.
4	Now decide where the two atoms with the higher priorities from steps 2 and 3 are in relation to each other. If both are above (or both are below) the double bond, then this is the Z-isomer. If one is above and the other is below the double bond, then this is the E-isomer.

table A Step-by-step guide to applying the *E-Z* naming system.



SUBJECT VOCABULARY

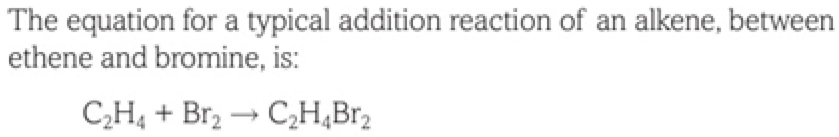
stereoisomers compounds with the same structural formula (and the same molecular formula), but with the atoms or groups arranged differently in three dimensions

geometric isomers compounds containing a C=C bond with atoms or groups attached at different positions

5A – 3 Addition reactions of alkenes

WHY DO ADDITION REACTIONS OCCUR?

In Topic 5A.1 we learned that the C=C double bond in an alkene is made up of two different single bonds, a sigma bond and a pi bond. Because the sigma bond electrons are more tightly held between the two carbon atoms, a sigma bond is stronger than a pi bond. This means that a double bond is stronger than a single bond, but it is not twice as strong.



The equation for a typical addition reaction of an alkene, between ethene and bromine, is:

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

You can see why this is called an **addition reaction**. Two molecules become one molecule. However, this equation does not show the mechanism of the reaction, i.e. how it occurs, in terms of the movement of electrons.

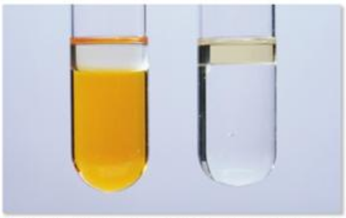
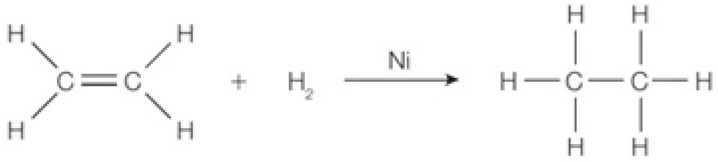


fig A The test for a C=C double bond. The tube on the left shows coloured bromine water with a layer of an organic compound on top. The tube on the right shows the mixture after shaking and leaving to settle. The bromine has been decolorised by the C=C bond.

HYDROGENATION

Hydrogenation is an addition reaction in which hydrogen is added to an alkene. The simplest example is the hydrogenation of ethene:

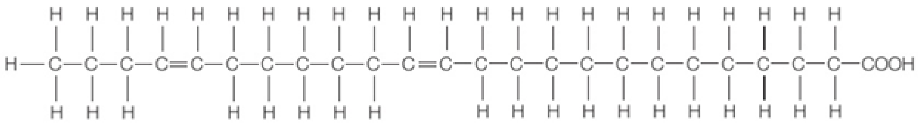


This reaction forms ethane, which is an alkane, and is done using heat and a nickel catalyst.

MANUFACTURE OF MARGARINE

Hydrogenation is extensively used in industry to manufacture margarine. Naturally occurring vegetable oils are unsaturated and so contain C=C double bonds. When these react with hydrogen, some of the C=C double bonds become C-C single bonds. This process changes the properties of the vegetable oil and converts it into a solid: margarine.

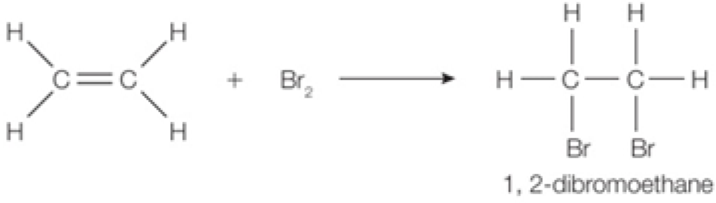
There is much concern about fats in the human diet, and many people consider that monounsaturated fats (one C=C double bond per molecule) and polyunsaturated fats (two or more C=C double bonds per molecule) are better than saturated fats (no C=C double bonds)

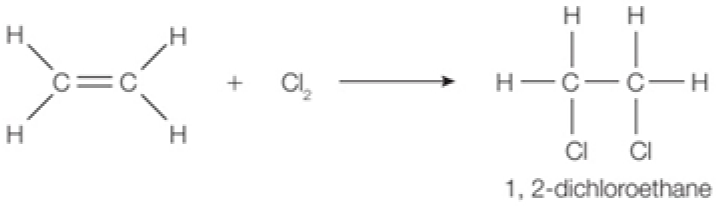


margarine

HALOGENATION

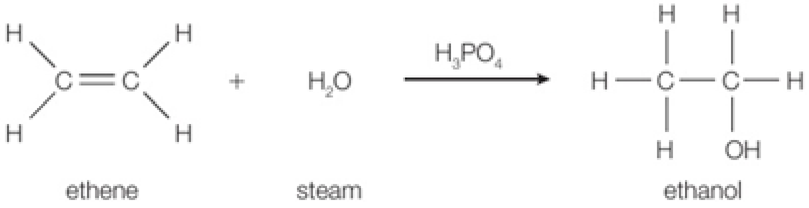
Reactions between alkenes and bromine are examples
of halogenation. The products of these reactions are dihalogenoalkanes. Reactions with chlorine are examples of





HYDRATION

Hydration should not be confused with hydrogenation. Hydration means adding water, but you should consider it as adding H and OH to the two atoms in a C=C double bond. This reaction is usually done by heating the alkene with steam and passing the mixture over a catalyst of phosphoric acid. The reaction with ethene can be represented as:



Unlike the hydrogenation of ethene, the hydration of ethene forms ethanol, which is a useful product. This reaction, and other similar ones to make propanol, are extensively used in industry.

ADDITION OF HYDROGEN HALIDES

Another example of an addition reaction is the addition of a hydrogen halide (often hydrogen bromide or hydrogen chloride) to form a halogenoalkane (more specifically, a bromoalkane or a chloroalkane). Here is one example:

$$CH_2{=}CH_2 + H{-}Br \rightarrow CH_3{-}CH_2Br$$

OXIDATION TO DIOLS

This heading suggests a different type of reaction to the previous ones. In fact, the reaction involves both addition and oxidation. A diol is a compound containing two OH (alcohol) groups.

The oxidising agent is potassium manganate(VII) in acid conditions (usually dilute sulfuric acid). Although you do not need to know the full details of how this reaction occurs, you can think of the reaction as oxidation followed by addition. The potassium manganate(VII) provides an oxygen atom (oxidation) and the water in the solution provides another oxygen atom and two hydrogen atoms, so there is the addition of two OH groups across the double bond.

The equation for the reaction of ethene can be represented like this:

$$CH_2{=}CH_2 + [O] + H_2O \rightarrow CH_2OH{-}CH_2OH$$

The symbol [O] represents the oxygen supplied by the oxidising agent. You do not need to show the potassium manganate(VII) in the equation or know how it supplies the oxygen for the oxidation. The product is ethane-1,2-diol.

SUBJECT VOCABULARY	
addition reaction	a reaction in which two molecules combine to form one molecule
hydrogenation	a reaction involving the addition of hydrogen
halogenation	a reaction involving the addition of a halogen
hydration	a reaction involving the addition of water (or steam)
diol	a compound containing two OH (alcohol) groups

During the reaction, the colour of the potassium manganate(VII) solution changes from purple to colourless. This colour change means that this reaction can be used like bromine to distinguish alkenes from alkanes (alkanes do not have double bonds and so are not oxidised in this way)

5A – 4 The mechanisms of addition reactions

BACKGROUND

We have already looked at reaction mechanisms with alkanes (initiation, propagation and termination). We saw how a curly half-arrow was used to represent the movement of a single electron. Now we can look in some detail at how addition reactions occur, which will involve the use of (full) **curly arrows** to represent the movement of a pair of electrons.

You already know that an alkene such as ethene has a pi bond, which is a region of high electron density (we could say that the molecule is electron rich around the C=C double bond). This makes an alkene molecule attractive to other species that are electron deficient, including molecules with polar bonds. Hydrogen bromide is a polar molecule because bromine is more electronegative than hydrogen, and can be shown with partial charges as:

$$\overset{\delta+}{H}{-}\overset{\delta-}{Br}$$

WHY DO ELECTROPHILES ATTACK ALKENES?

When a hydrogen bromide molecule approaches an ethene molecule, the slightly positive end of the HBr molecule is attracted to the electrons in the pi bond in C=C. The HBr molecule is described as an electrophile when it does this. Remember that **electrophiles** attack centres of negative charge.

The curly arrows used in reactions of this type must either:

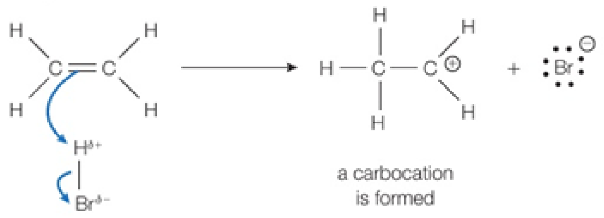
- start from a bond and move to an atom, or
- start from a lone pair of electrons and move to an atom.

ELECTROPHILIC ADDITION OF HYDROGEN HALIDES

The complete name of this reaction is **electrophilic addition**. It involves addition and it involves attack by an electrophile. This is the mechanism of the reaction between ethene and hydrogen bromide.

This kind of bond breaking is called **heterolytic fission** (compare this with homolytic fission in the substitution reactions of alkanes).

Step 1

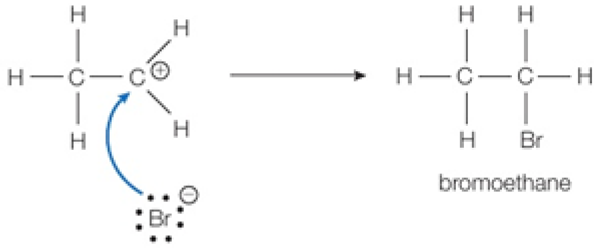


a carbocation is formed

In this step, two ions are formed. The positive ion has its charge on a carbon atom, so it is known as a **carbocation**.

Step 2

The two oppositely charged ions attract each other and react to form a new covalent bond as one of the lone pairs of electrons forms a covalent bond with the carbon atom in the carbocation.

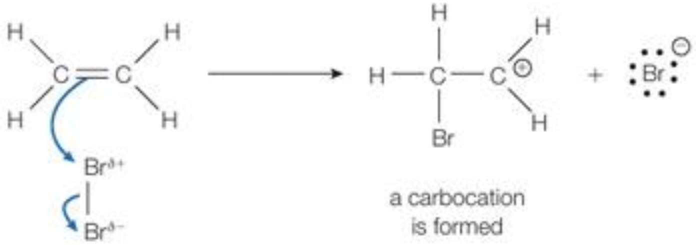


bromoethane

ELECTROPHILIC ADDITION OF HALOGENS

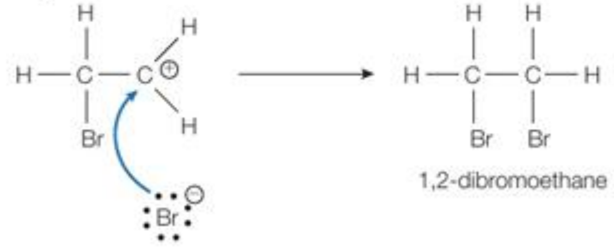
This reaction is very similar to the reaction of hydrogen halides. The only difference is that the attacking bromine molecule does not have a polar bond. However, as it approaches the C=C bond, the electrons in the pi bond repel the electrons in the Br-Br bond and induce (cause) the molecule to become polar. After that happens, the mechanism is just the same as for hydrogen bromide.

Step 1



a carbocation is formed

Step 2

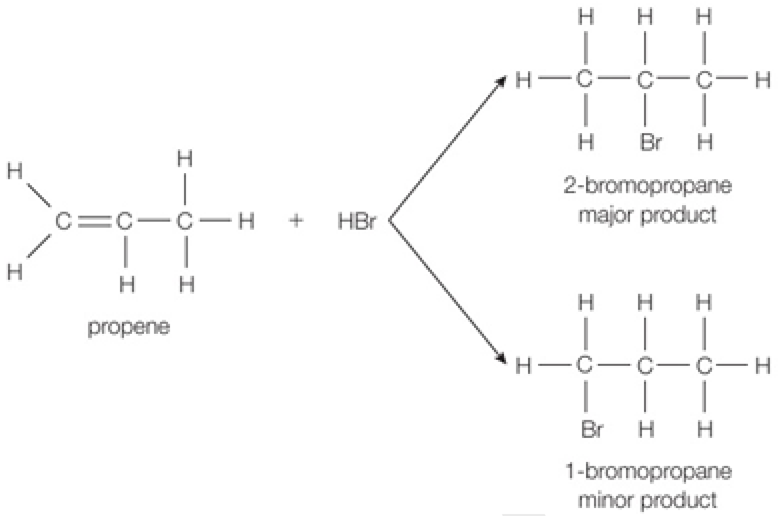


1,2-dibromoethane

ASYMMETRICAL MOLECULES

There is one more point to consider before leaving this topic. When a molecule such as H-Br or Br-Br reacts with ethene in an addition reaction, there can only be one product. If both the alkene and the attacking molecule are asymmetrical, then there are two possible products. This is because the atoms in the attacking molecule can be added in two different places

A good example is the reaction between propene and hydrogen bromide.



In reactions of this type, one product is formed in greater amounts than the other. There is a major product and a minor product. Now we need to explain why. We can do this by considering the two possible carbocations formed in Step 1 of the reaction.

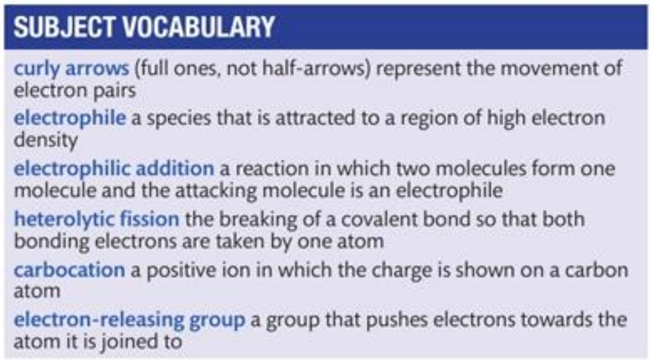

$CH_3-\overset{\oplus}{C}H-CH_3$

structure A


$\overset{\oplus}{C}H_2-CH_2-CH_3$

structure B

A general principle to consider is that a carbocation in which the charge can be spread over more atoms is more stable than one in which there are fewer atoms available to spread the charge. Alkyl groups are **electron-releasing groups**, so when there are two of them, the charge on the carbocation is spread more than when there is only one. In some reactions, there might be a tertiary carbocation (with three alkyl groups joined to the carbon atom with the positive charge), and this would be more stable than a secondary carbocation.



SUBJECT VOCABULARY	
curly arrows	(full ones, not half-arrows) represent the movement of electron pairs
electrophile	a species that is attracted to a region of high electron density
electrophilic addition	a reaction in which two molecules form one molecule and the attacking molecule is an electrophile
heterolytic fission	the breaking of a covalent bond so that both bonding electrons are taken by one atom
carbocation	a positive ion in which the charge is shown on a carbon atom
electron-releasing group	a group that pushes electrons towards the atom it is joined to

5B – 1 Polymerization reactions

ALKENES USED IN ADDITION POLYMERISATION

Many compounds containing the C=C double bond can be polymerised. There is no need to know the mechanisms of these reactions, but you should describe them as addition reactions because the alkene molecules add together in vast numbers to form the polymer. You also do not need to know the exact conditions used in polymerisation reactions, but normally they use a combination of high pressure and high temperature, which varies depending on the polymer.

NAMING POLYMERS

When alkene molecules are used in polymerisation, they are ofter referred to as monomers. The standard way to name a polymer is by writing 'poly', followed by the name of the monomer in brackets. The obvious example is the use of ethene to form poly(ethene). Most people abbreviate this name to polythene. Even though the polymer formed is saturated, the 'ene' ending is still used.

Table A shows information about some common polymers.

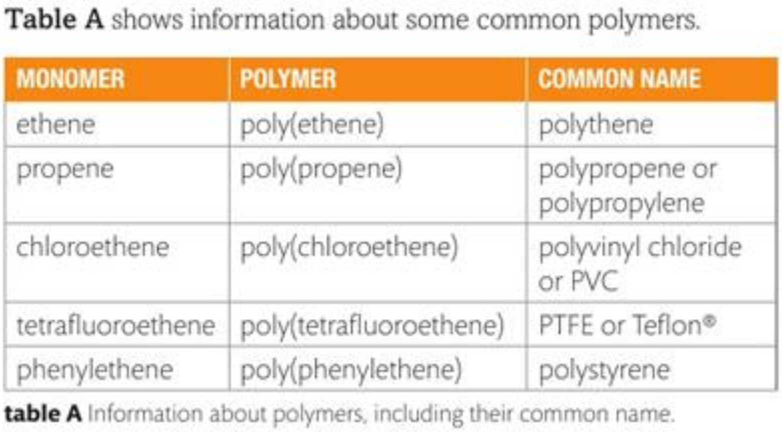


Table A shows information about some common polymers.

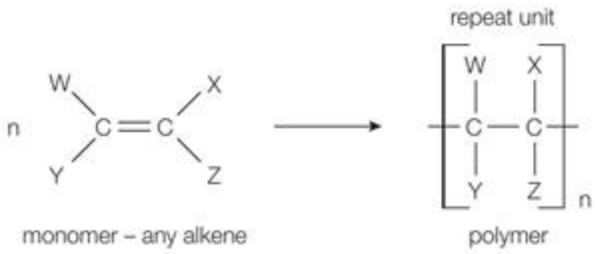
MONOMER	POLYMER	COMMON NAME
ethene	poly(ethene)	polythene
propene	poly(propene)	polypropene or polypropylene
chloroethene	poly(chloroethene)	polyvinyl chloride or PVC
tetrafluoroethene	poly(tetrafluoroethene)	PTFE or Teflon®
phenylethene	poly(phenylethene)	polystyrene

table A Information about polymers, including their common name.

EQUATIONS FOR POLYMERISATION REACTIONS

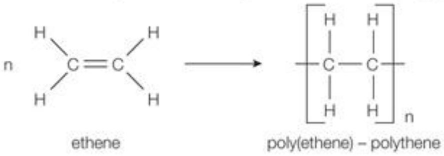
Because the polymers formed do not have a fixed molecular formula (their molecular masses can be anything from many tens of thousands to millions), we need to find a different way to show what happens in the reaction. The usual way to do this is to use the letter 'n' to represent the number of monomer molecules reacting, then to show the **repeat unit** of the polymer inside a bracket (curved or square).

A general equation that you can modify for use with all addition polymerisation reactions is:

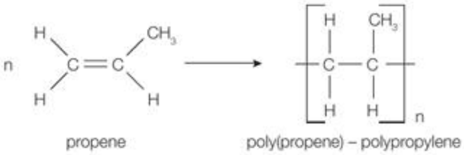


EXAMPLES OF EQUATIONS

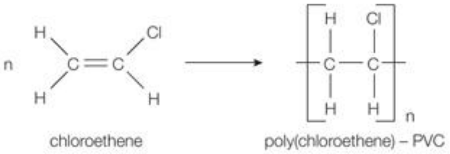
Here is the equation showing the formation of poly(ethene):



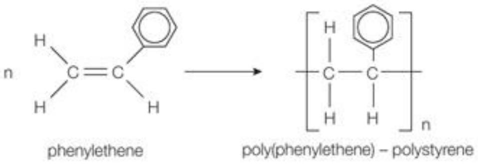
Here is the equation showing the formation of poly(propene):



This equation shows the formation of poly(chloroethene), better known as PVC:



Finally, this equation shows the formation of poly(phenylethene), better known as polystyrene:

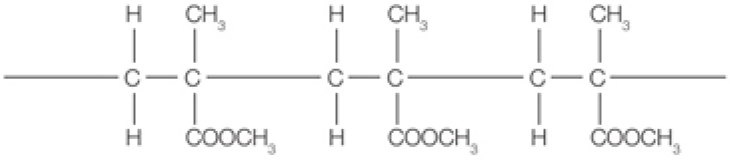


IDENTIFYING THE MONOMER

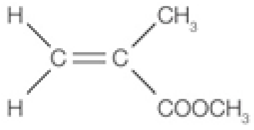
If you are given the repeat unit of a polymer, or a section of the polymer that contains several repeat units, you can work out the structure of the corresponding monomer.

This is part of the structure of poly(methyl methacrylate), better known as Perspex:

This is part of the structure of poly(methyl methacrylate), better known as Perspex:



There are no brackets and no subscript n, because this shows part of the structure and not just the repeat unit. You can see that on alternate carbon atoms in the chain, there are two hydrogen atoms, one methyl group and one $COOCH_3$, group. It doesn't matter if you don't recognise the $COOCH_3$, group, you can still work out the monomer structure. The monomer structure is:



methyl methacrylate

SUBJECT VOCABULARY

monomers the small molecules that combine together to form a polymer

repeat unit the set of atoms that are joined together in large numbers to produce the polymer structure

5B – 2 Dealing with polymer waste

BACKGROUND

A hundred years ago, traditional materials used to make everyday objects were substances such as wood, metal, glass, wool and paper. Although these materials are still used today, we have become increasingly reliant on polymers (plastics) for many everyday objects. Reasons for the increasing use of polymers include the following.

fig A There must be a way to reduce how many single-use plastic bottles of water are thrown away.

- They can be manufactured on a large scale in a variety of complex shapes and with a wide range of physical properties. Think of plastic bottles that can be rigid when used to hold bleach or flexible to hold washing-up liquid.
- They are often lighter in weight than traditional alternatives. Think of milk in a glass bottle compared to a plastic bottle.
- They are unreactive and so they can be used to contain many substances safely for long periods. Think of how metals corrode and wood rots.

SOLUTIONS TO POLYMER WASTE

There are several ways to limit the problems caused by the disposal of polymer waste.

- One way is not to use polymers unnecessarily. In some countries, the use of single-use plastic bags by supermarkets has been banned.

- Another way is recycling, which means converting the polymer waste into new materials that are useful. For example, poly(ethylene terephthalate), better known as PET or PETE, is widely used in plastic bottles, and this polymer is now recycled on a large scale to make carpets.

- **Incineration** (burning the polymers) is widely used. Although this method gets rid of the polymer waste, unfortunately it leads to the formation of carbon dioxide (a greenhouse gas) and also some toxic gases.

- Biodegradable polymers are considered by many scientists to be worth developing.

INCINERATION

The elements present in polymer waste are mostly hydrogen and carbon, so they can be used as fuels, in a similar way to other hydrocarbons. An incinerator takes in polymer waste and converts it into heat energy that can be used to heat homes and factories, or used to generate electricity. There is very little solid waste left after incineration, but that is because most of the atoms in the polymers end up in gaseous products which pass into the atmosphere via a chimney.

BIODEGRADABLE POLYMERS

Traditional plastics put into landfill do not break down. The idea of using **biodegradable** polymers (sometimes described as biopolymers) is to allow them to be broken down by microbes in the environment. This sounds like a good idea, and some of them are used on a small scale in medicine (for sutures (stitches) and in drug delivery).

However, there are some disadvantages.

- They are often made from plant material, so there is the same issue to consider as with biofuels, that is, land is needed to grow the plants.

- They are designed to break down in the environment, so when they do, the hydrogen and carbon atoms they contain cannot be directly used.

SUBJECT VOCABULARY

recycling converting polymer waste into other materials that are useful
incineration converting polymer waste into energy by burning
biodegradable a biodegradable substance is one that can be broken down by microbes

▲ **fig B** This incineration plant in the Maldives gets rid of polymer waste, but what is coming out of the chimney?

▲ **fig C** This looks like an ordinary plastic cup, but it is actually biodegradable and made from plant material.

Revision questions

1. This question is about alkenes.

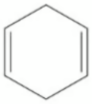
Which of these has the molecular formula C_6H_{10}?

☒ **A**

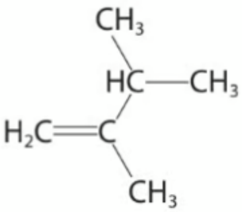
☒ **B**

☒ **C**

☒ **D**



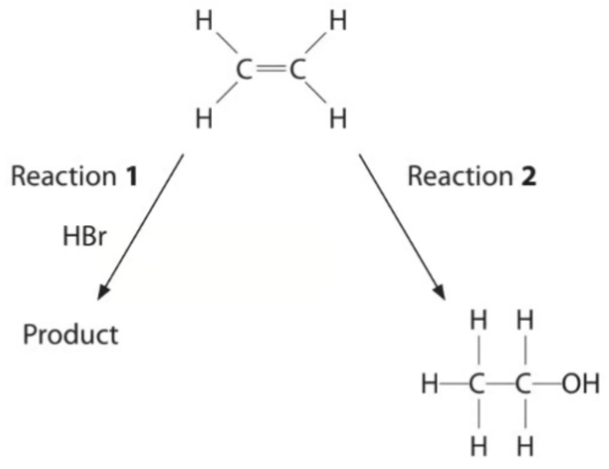
2. What is the systematic name of this alkene?



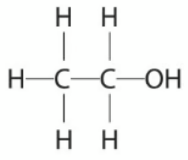
☐ **A** 2-methylpent-1-ene
☐ **B** 3-methylpent-1-ene
☐ **C** 2,3-dimethylbut-1-ene
☐ **D** 2,3-dimethylbut-3-ene

3.

Two reactions of ethene are shown.

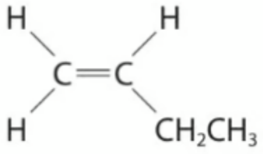


Complete the table.

Reaction	Reagent and condition	Product
1	HBr at room temperature	
2		

5.

But-1-ene has the structure



i) Draw the structure of the polymer formed when but-1-ene polymerises.
Include **two** repeat units.

ii) Calculate the number of molecules in 70.0 g of but-1-ene.
[Avogadro constant = 6.02×10^{23} mol^{-1}]

6. This question is about alkenes with the molecular formula C_5H_{10} .

Draw the **skeletal** formulae of three **branched** chain alkenes with the molecular formula C_5H_{10} .

7.

A sample of pent-1-ene, with a mass of 1.33 g, is warmed to 60 °C in a sealed container. The volume of the container is 500 cm^3

Calculate the pressure inside the container.
Include units and give your answer to an appropriate number of significant figures.

[Gas constant (R) = 8.31 J mol^{-1} K^{-1}]

8. Pent-2-ene reacts with hydrogen bromide, HBr, to form two bromoalkanes.

Complete the diagram to show the mechanism for the formation of 2-bromopentane in this reaction.
Include curly arrows, and relevant lone pairs and dipoles.