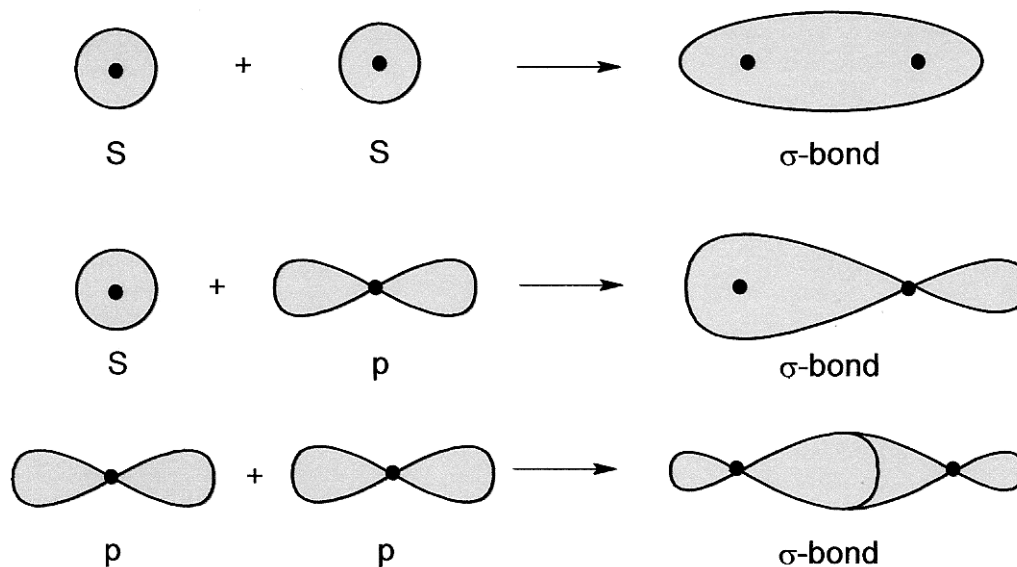
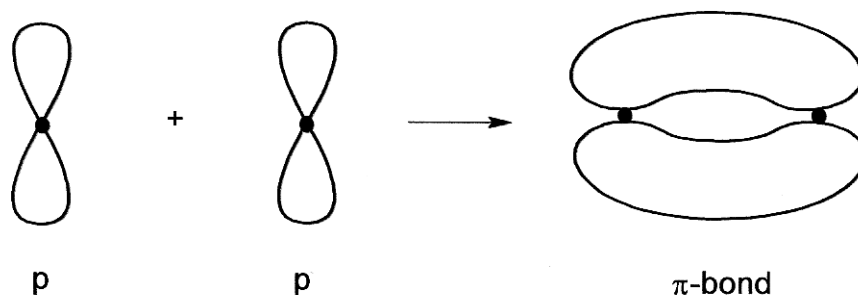


Types of Covalent Bond

Sigma-bonds (σ -bonds) are covalent bonds that form between two atoms with the bonding electron concentrated directly between the two atomic nuclei. They may form, for example, between two spherical s-orbital electrons, an s-orbital and an end-on p-orbital, or two p-orbitals end-on to each other. The diagram below illustrates these types of σ -bond. The black dots indicate the positions of the atomic nuclei.



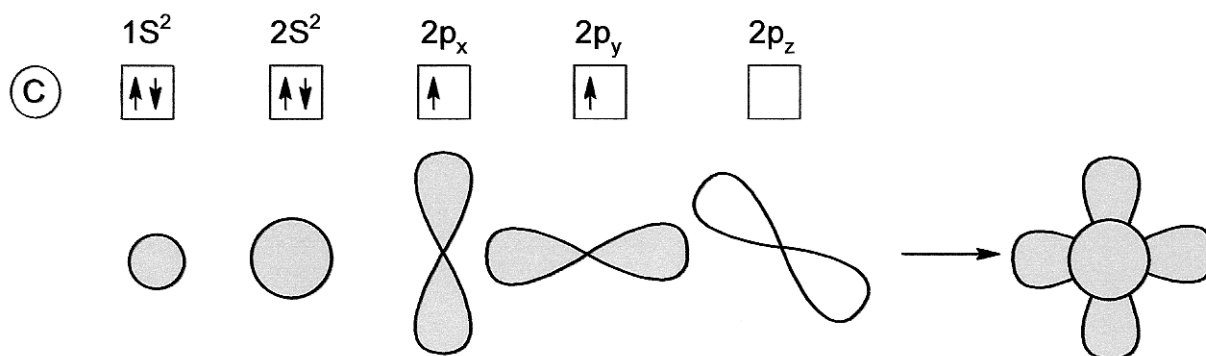
Pi-bonds (π -bonds) are covalent bonds that form when p-orbitals overlap side-on, such that there are regions of overlap above and below the axis joining the two nuclei, and it is in these off-axis regions that the electron density is concentrated.



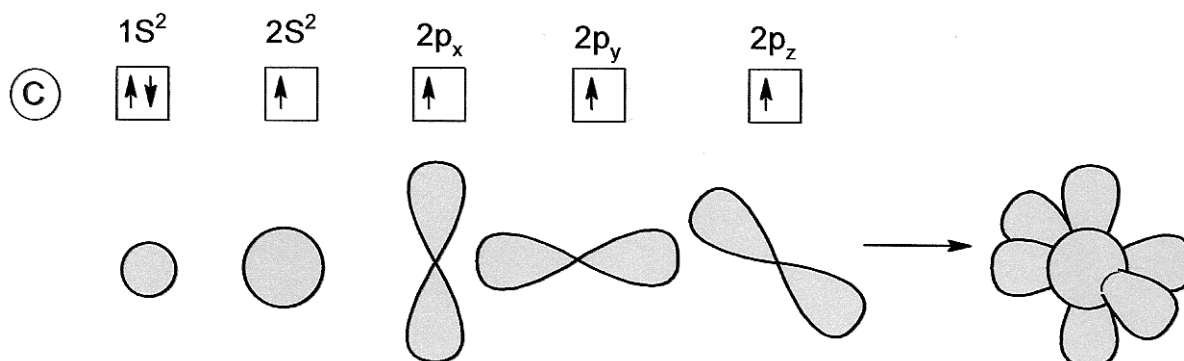
Sigma-bonds are stronger than pi-bonds, because the electron density in a sigma-bond is concentrated between the two positively charged nuclei, which are held together by their attraction to the intervening electrons. In a pi-bond, however, the electron density is not concentrated directly between the two positive nuclei and so they are less strongly bound. Sigma bonds form first, but a second bond in a double bond will usually be a pi-bond, since geometrically a pi-bond can accommodate a sigma-bond in-between its lobes (see the 'bonding in ethene' example).

The Electron Configuration in Carbon

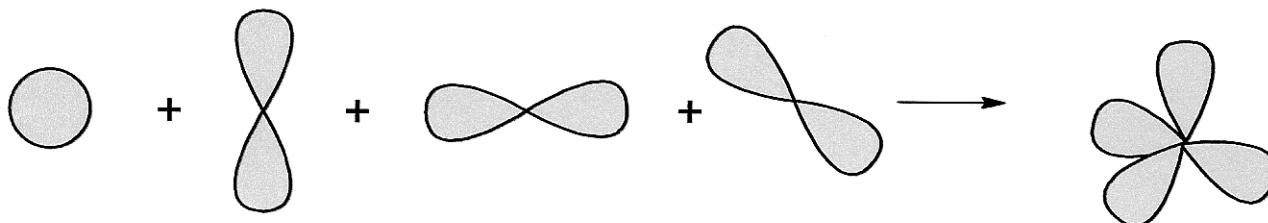
When C is in its ground state it has the following electron configuration with 2 unpaired electrons:



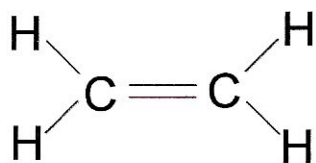
So how can C form 4 covalent bonds? When bonding C is in excited state with one 2s electron promoted to the 2p subshell:



So how does C form 4 covalent bonds with a tetrahedral arrangement? Electron repulsion reconfigures the electron clouds, in fact the 2s and the three 2p orbitals hybridise to form 4 equivalent sp^3 hybrid orbitals separated by 109.5° :

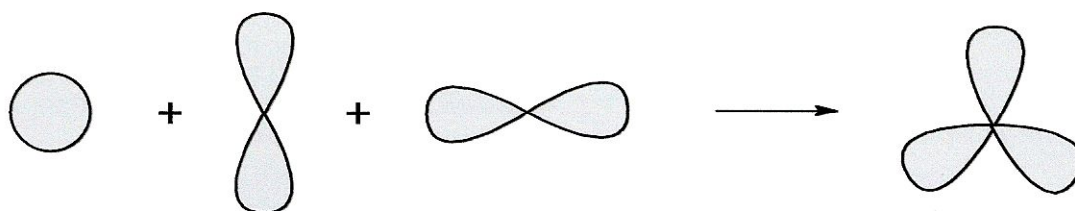


What about when C forms C=C bonds (is in ethene) or C to C triple bonds (as in ethyne)?

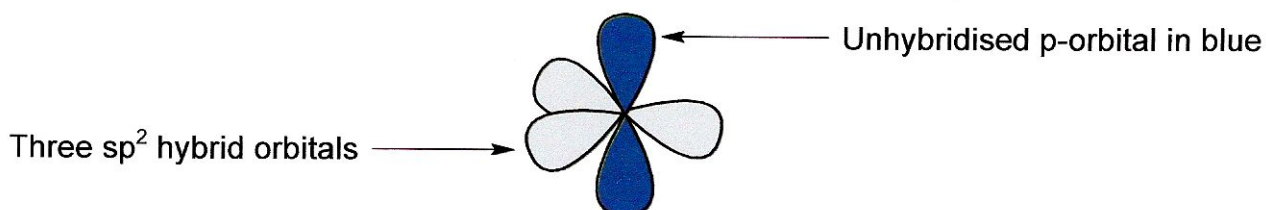


In ethene three of the bonding orbitals are equivalent and separated by 120° . The fourth contributes to the double bond.

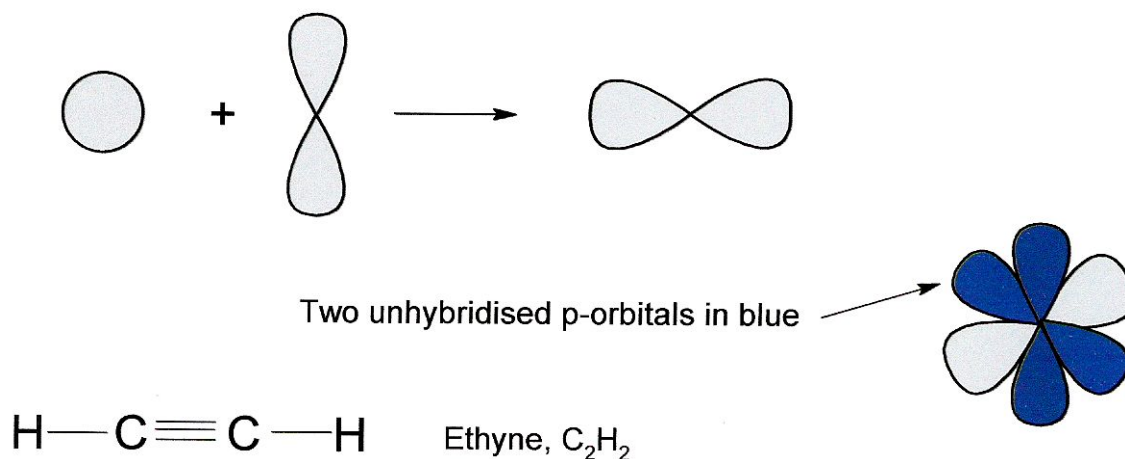
When C is in its excited state, the 2s electron can hybridise with two of the 2p electrons, to form three equivalent sp^2 hybrid orbitals, separated from each other by 120° :



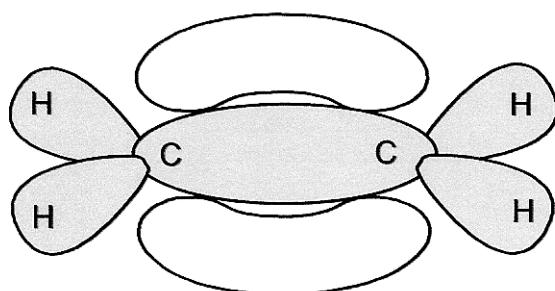
This leaves the remaining p orbital free to contribute to the C=C bond:



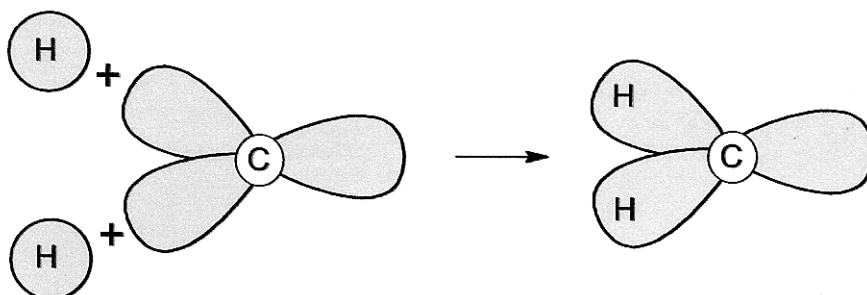
Similarly one 2s electron can hybridise with one 2p electron to form two equivalent sp hybrid orbitals (separated by 180°), allowing the two remaining non-hybridised 2p orbitals to contribute to the C to C double and triple bonds, as in ethyne for example:



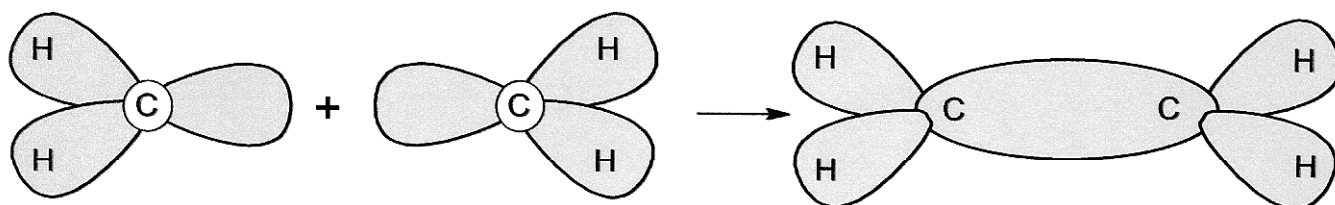
The Molecular Orbitals of Ethene:



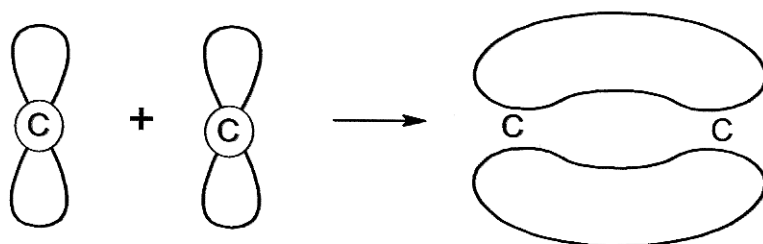
Formation of σ -bonds between H s-orbitals and C sp^2 hybrid orbitals:



Formation of σ -bonds between C sp^2 hybrid orbitals:



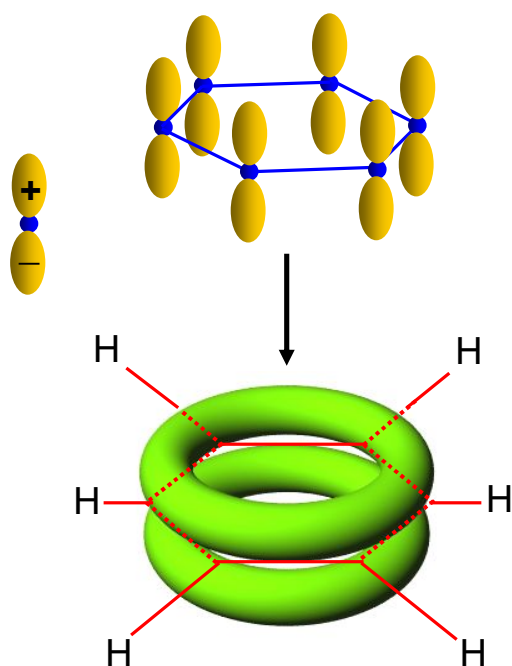
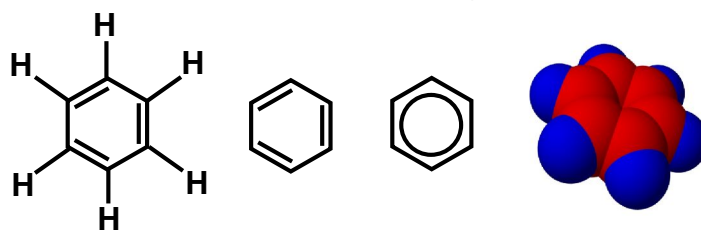
Formation of π -bonds between C p-orbitals:



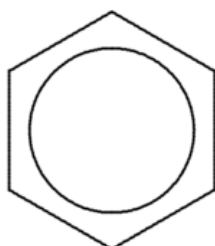
Bonding in benzene

Benzene (C_6H_6) is the most basic arene from which many other aromatic compounds are derived. Arenes are hydrocarbons with ring-systems containing delocalised pi-electrons. They are not to be confused with cycloalkanes or cycloalkenes which do not have delocalised electrons. Aromatic compounds are compounds that contain ring-systems of delocalised electrons and include the arenes and their derivatives. Aromatic compounds were so-named because many of these compounds have distinctive aromas.

There are different ways of representing the structure of benzene:



In exams, draw benzene using the skeletal formula on the right. Examiners may not like to see it drawn with alternating single and double bonds!



In benzene six C atoms are joined together in a symmetric hexagonal ring. Each of these 6 C atoms is joined to its two neighbours by σ -bonds between sp^2 hybrid orbitals. The third lobe of each sp^2 hybrid orbital is σ -bonded to the 1s orbital of a H atom. This leaves one p orbital unaccounted for on each C atom. The lobes of this orbital are perpendicular to the plane of the ring, one above and the ring and one below. The lobes of these p-orbitals overlap sideways on to form π -bonds with those on the neighbouring C atoms. However, since each p-orbital contains a single electron, this means that there are only 6 electrons to form 6 covalent bonds between all the C atoms. Clearly this can not happen in the normal sense. There are not enough electrons to fill the resultant molecular orbital. The result is that the p-electrons become delocalised, so that they are free to move about the ring. The result is a delocalised π -electron ring system.

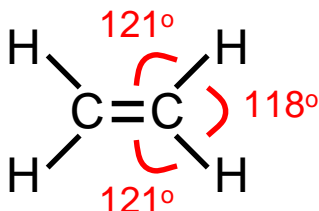
Hydrocarbons: Alkenes

Alkenes are unsaturated hydrocarbons – that is they contain one or more C=C double bonds.

General formula: straight chain alkenes with one C=C bond form an homologous series with the general formula C_nH_{2n} .

Structure of alkenes:

Ethene is a flat planar molecule. One might expect the angles between bonds around each C atom to be 120° . However, the H-C-H bond angles are actually 118° because the double C=C bond contains 4 electrons and so repels more strongly than a single bond containing 2 electrons.



Q.1. Draw a dot-cross diagram for ethene.

N.B. There is no free rotation about the C=C bond, the double bond is just too rigid. This can lead to *cis-trans* isomerism in many compounds containing a double C=C bond.

Q.2. but-2-ene exists as *cis-* and *trans-* isomers. Draw the structural formulae for *cis-but-2-ene* and *trans-2-but-ene*.

Physical properties of alkenes:

The physical properties of alkenes are very similar to those of alkanes, since the C=C double bond has no effect on the van der Waal's intermolecular forces and so does not affect melting and boiling points significantly. Like alkanes, alkenes are not soluble in water, since they are non-polar. Melting and boiling points increase with chain length. Ethene, propene and butene are gases at room temperature, pent-1-ene boils at 30.0°C and so is generally a volatile liquid at room temperature. Cyclohexene is a liquid at room temperature.

How alkenes react:

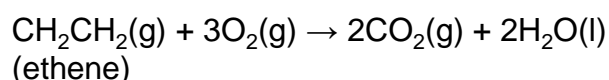
The C=C double bond has a major effect on the chemical properties of alkenes. The C=C bond is almost twice as strong as a single C-C bond, so one might assume that alkenes are less reactive. However, alkenes are much more reactive for the following reasons:

- The bond energy for the C=C double bond is 612 KJ mol⁻¹, and for C-C it is 347 KJ mol⁻¹. The C=C bond consists of a σ -bond and a π -bond; this σ -bond is similar in strength to the C-C σ -bond, which means that the π -bond is quite a bit weaker, with a bond energy of (612-347) 265 KJmol⁻¹. It is relatively easy for this π -bond to break in a chemical reaction, leaving the σ -bond intact. In most reactions this is what happens, the π -bond breaks and reacts, whilst the C chain remains unbroken.
- When the π -bond breaks, each C atom is left short of one electron, and so these Cs are highly reactive and can easily attach to new groups which are said to be added across the double bond in an addition reaction.
- The C=C bond is electron rich (4 electrons in a small volume) and so is easily attacked by positively charged reagents called electrophiles ('electron loving'). Such an electrophile can be added across the double bond in an electrophilic addition reaction. Most alkene reactions are electrophilic additions.

Q.3. Butene forms two structural isomers in which the C=C double bond occupies different positions in the chain. Draw and name these two isomers.

Reactions of Alkenes:

Combustion: alkenes burn in air (oxygen) to release energy, in the same way that alkanes burn:

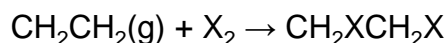


However, alkenes are not used as fuels, because their chemical reactivity makes them useful in the manufacture of useful substances, such as plastics.

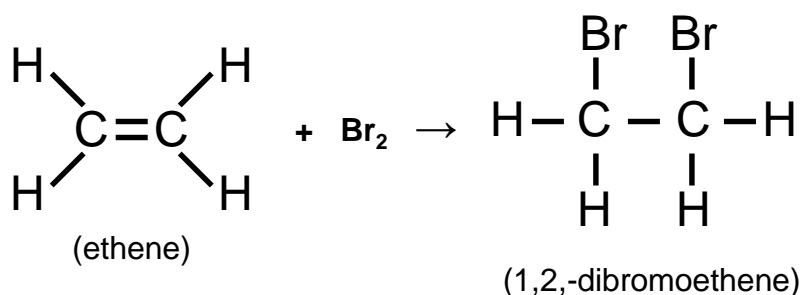
Electrophilic Addition Reactions:

Reaction of alkenes with halogens:

Alkenes rapidly react with chlorine gas, or bromine and iodine (in an organic solvent), to give dihalogenoalkanes.



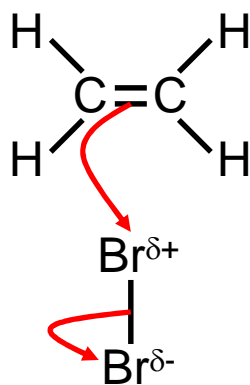
Where X_2 is any halogen, e.g.



Test for a double bond (test for unsaturation): when a few drops of bromine solution (reddish-brown) are added to an alkene, the solution is decolourised as the bromine reacts because halogenoalkanes are colourless.

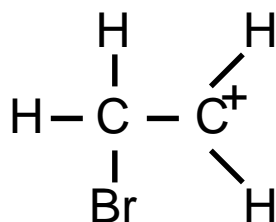
Reaction Mechanism: the mechanism for this halogenation, or electrophilic addition reaction proceeds by the following steps:

1. The electrophile attacks: Br_2 molecules can have instantaneous-induced dipoles, with one end of the molecule slightly positive, the other slightly negative: $\text{Br}^{\delta+}-\text{Br}^{\delta-}$. The $\delta+$ end of this dipole is attracted to the electron-rich double bond in ethene – the Br_2 dipole is an electrophile.
2. The double bond responds. The electrons in the double bond are attracted to the $\text{Br}^{\delta+}$. They repel the electrons in the $\text{Br}-\text{Br}$ bond, and so stabilise and strengthen the bromine dipole.



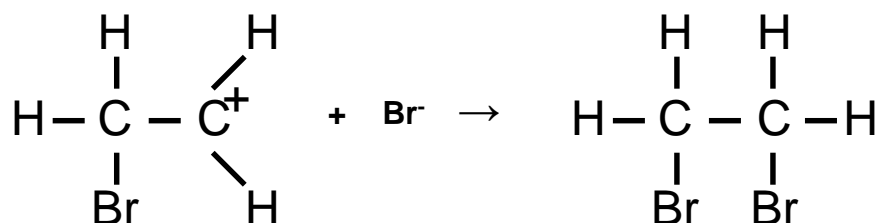
Red arrows indicate movements of electron pairs.

3. A positive ion (carbocation) is formed. Two of the electrons from the double bond form a bond with the $\text{Br}^{\delta+}$ and the other bromine atom becomes a Br^- ion, as the electrons completely leave the $\text{Br}-\text{Br}$ bond. This leaves a carbocation, in which the C atom that is NOT bonded to the bromine has the positive charge (think about it, this C is electron deficient).



(a carbocation)

4. The Br^- ion is attracted to the C with the positive charge. Br^- is the only negative ion present in the solution and is strongly attracted to the $-\text{C}^+$, so this reaction stage is very rapid. The Br^- contributes two electrons to form the $\text{C}-\text{Br}$ bond.



(a carbocation)

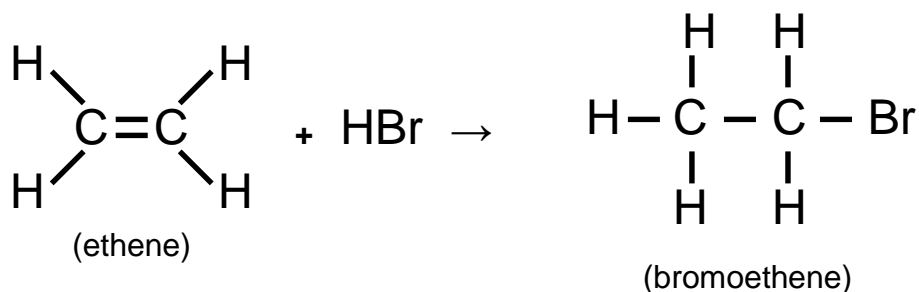
(1,2,-dibromoethene)

Reaction summary: the reaction took place in two main stages –

- Formation of a carbocation by electrophilic addition.
- Rapid reaction with a negative ion.

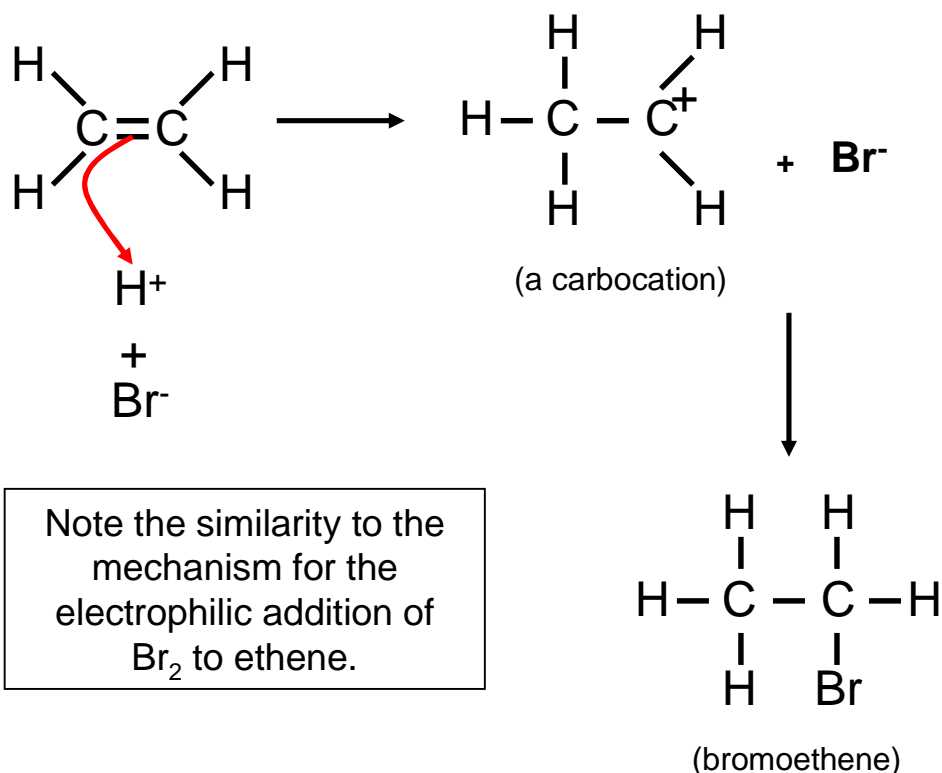
Q.4. In what ways does the reaction of alkenes with halogens differ from the reaction of alkanes with halogens?

Reaction with hydrogen halides. HCl, HBr and HI add on across the C=C double bond to form a halogenoalkane. E.g.



Mechanism: electrophilic addition

•The bond in hydrogen bromide breaks heterolytically, that is both bonding electrons go to one atom (Br) to form H⁺ and Br⁻. The H⁺ ion has one whole positive charge and so is a good electrophile. The H⁺ is attracted to the electrons in C=C double bond and forms a bond with two of the four bonding electrons in this double bond. This produces a positively charged carbocation that is rapidly attacked by the Br⁻ ion:



Q.5. When the double bond is not in the middle of the chain, there are two possible products because the bromide could add to either C in the double bond. Addition of Br₂ to propene produces both 2-bromopropane and 1-bromopropane (though mostly 2-bromopropane). Draw the structure for propene, the two intermediate carbocations and the two end products.

Reaction with Water:

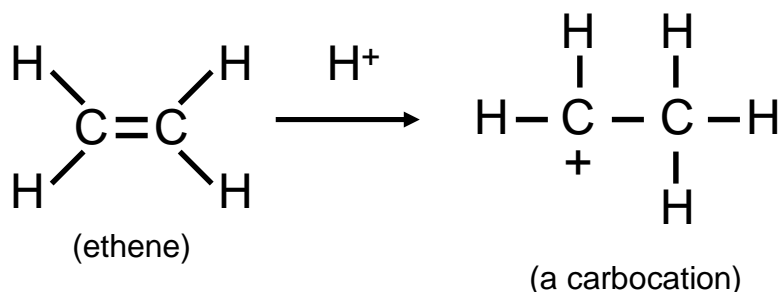
Water, in the form of steam, also adds across the C=C double bond in alkenes, in the presence of an acid catalyst, such as phosphoric acid (H₃PO₄). This process is carried out on an industrial scale to manufacture alcohols.

Mechanism: electrophilic addition:

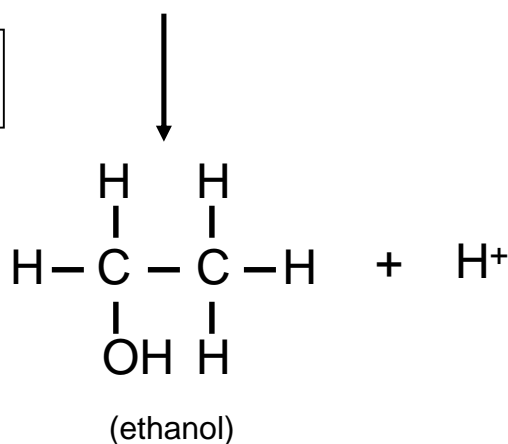
e.g. ethene + steam:

•A H⁺ (from the phosphoric acid) acts as an **electrophile** and adds to ethene to form a carbocation.

•The slightly negative O of the polar water molecule is attracted to the + charge on the carbocation, adding an –OH group to the carbocation, regenerating a proton, H⁺.

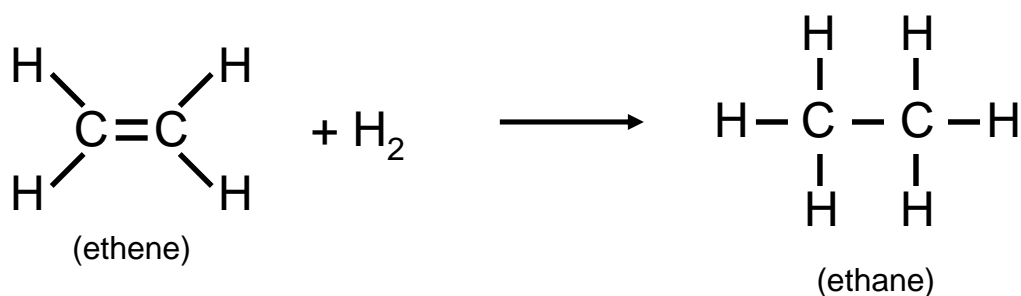


Q.6. How does this reaction mechanism tell you that H⁺ is acting as a catalyst?



Addition of hydrogen:

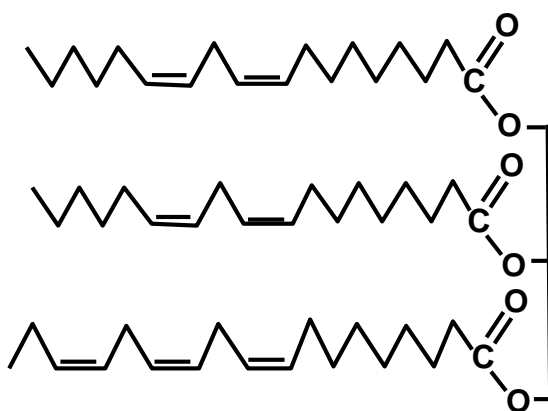
Hydrogen adds across the double bonds of alkenes, turning them into alkanes. This reaction occurs at room temperature and pressure in the presence of a highly porous nickel catalyst (called Raney nickel). E.g. the addition of hydrogen to ethene:



This addition reaction of hydrogen to alkenes is used commercially in the manufacture of margarine from vegetable oils. Vegetable oils are fats (lipids) containing long hydrocarbon chains with several C=C double bonds. Oils with several double bonds are polyunsaturated. Oils with more double bonds pack together less closely (because the double bonds put 'kinks' in the C chains, making them fit together less well. This lengthens the inter-chain distance, making the van der Waals forces between the chains longer and weaker, reducing the melting point, so that these oils are liquids at room temperature.

Adding hydrogen reduces the number of C=C double bonds, allowing the chains to pack closer together, strengthening the van der Waals forces between neighbouring chains, and so raising the melting point. Margarine is made by adding hydrogen to vegetable oils using a powdered nickel catalyst (which is later filtered off) at about 420 K and 500 kPa pressure.

Vegetable oils contain more C=C double bonds than animal fats which are more saturated (a fully saturated hydrocarbon has a maximum H:C ratio and no C=C double bonds). Thus, animal fats have high melting points and are solids at room temperature. Polyunsaturated fats are healthier. The trick is not to saturate all the double bonds, but just enough to make the oil semi-solid and spreadable.

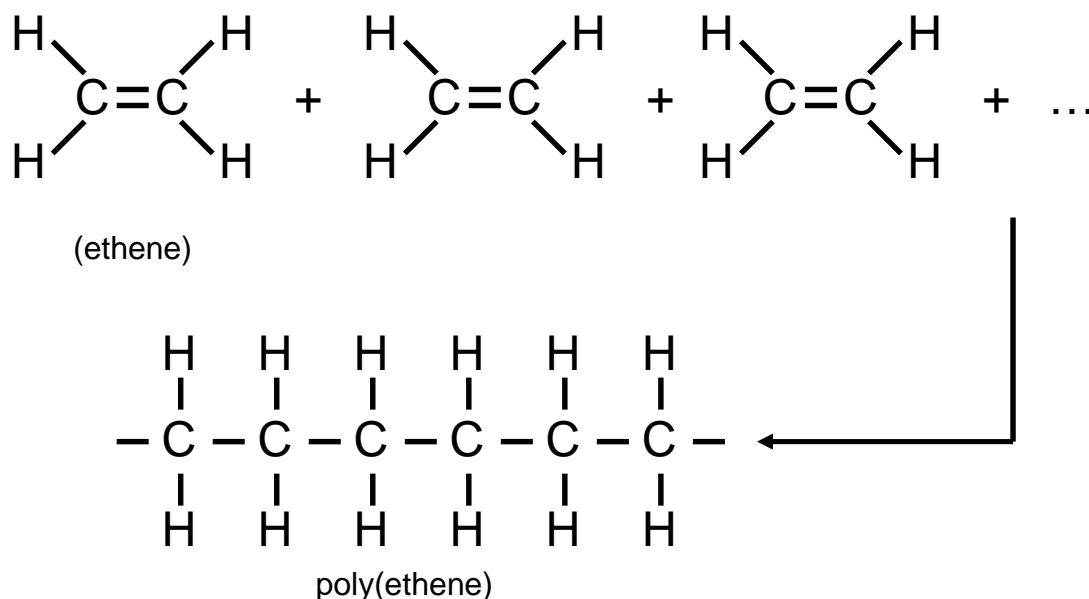


A typical unsaturated vegetable oil
before reaction with hydrogen

Addition Polymerisation of Alkenes

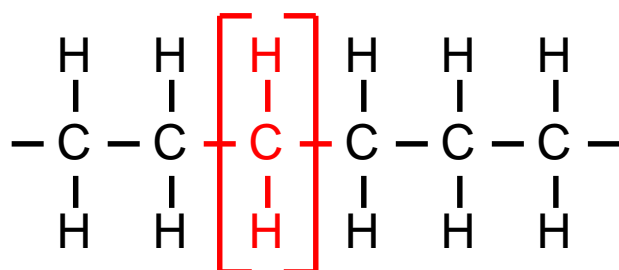
Alkenes can polymerise, that is they can join together end-to-end to form long chains or polymers (with molecular masses up to 1 000 000).

For example, ethene can act as a monomer and polymerise into poly(ethene) (polythene):



N.B.

- Although ethene (C_2H_4) is the monomer, the repeat unit is $-\text{CH}_2-$
- Although the polymer is called poly(ethene) it is in fact a very long alkane.
- The reaction is addition polymerisation because the ethene monomers are added together.



The repeat unit

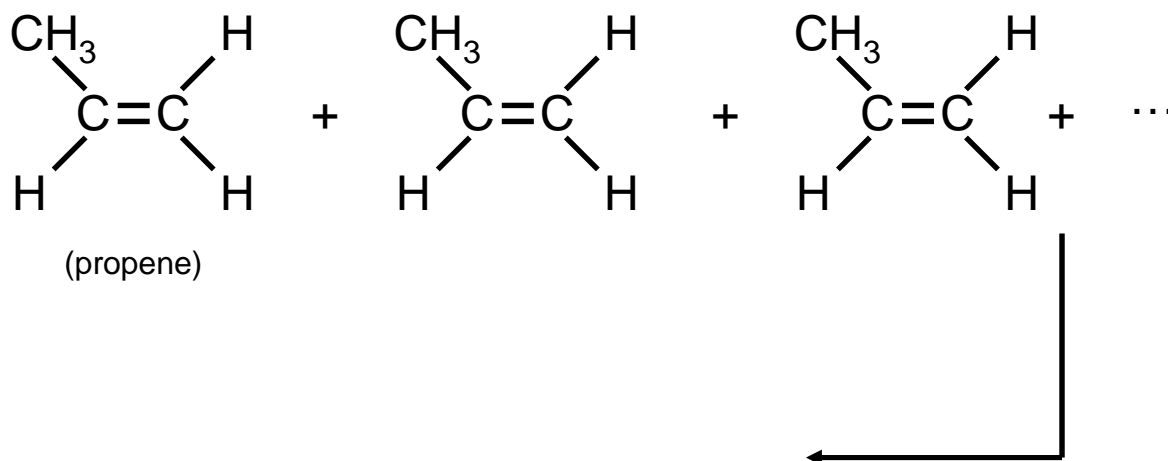
The repeat unit is the smallest group of atoms that is repeated over and over.

Different forms of poly(ethene) can be manufactured by varying the temperature, pressure and catalyst used. These poly(ethenes) differ in chain length and also in the degree of branching.

Poly(propene)

Poly(propene) is formed from polymerisation of the monomer **propene**.

Q.7. Complete the equation below for the polymerisation of propene. What is the repeat unit of this polymer.



Problems with Plastics:

Most plastics are only degraded slowly by micro-organisms and many not at all – they are **non-biodegradable**. This problem gets worse with time as more plastic litter accumulates. Plastics may take hundreds of years to decompose.

Solutions: reduce the amount of plastic used or recycle it!

Mechanical recycling: Plastics are separated into types, washed and ground up into small pellets. These pellets are then **melted and remoulded**. Plastics drinks bottles are recycled mechanically to make fleece clothes. Problem: this can only be done a limited number of times, since each time it is heated, some of the polymer chains in the plastic are broken, so that the chains become shorter each time, affecting the plastics properties.

Feedstock recycling: The plastics are heated until the polymers break down into their monomers, which can be used to make new polymers. (Feedstock refers to chemicals that are used as ingredients in the industrial synthesis of other chemicals).

Burning: Some plastics, like poly(ethene) can be burnt for fuel. Some produce toxic fumes, like HCl(g) from Cl-containing plastics like PVC. In the process of fume **scrubbing**, the fumes are passed through water → hydrochloric acid, which is neutralised with sodium hydroxide.

Some polymers in everyday use. The repeat units are shown in red brackets.

Monomer	Polymer	Systematic chemical name	Common name or trade name (in capitals)	Typical uses
$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\left[\text{CH}_2\right]_n$	poly(ethene)	Polythene polyethylene ALKATHENE	Washing-up bowels, plastic bags
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}=\text{CH}_2 \end{array}$	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_2 \end{array}\right]_n$	poly(propene)	polypropylene	rope
$\begin{array}{c} \text{Cl} \\ \\ \text{CH}=\text{CH}_2 \end{array}$	$\left[\begin{array}{c} \text{Cl} \\ \\ \text{CH}-\text{CH}_2 \end{array}\right]_n$	poly(chlorethene)	polyvinylchloride PVC	Vinyl records
$\begin{array}{c} \text{CN} \\ \\ \text{CH}=\text{CH}_2 \end{array}$	$\left[\begin{array}{c} \text{CN} \\ \\ \text{CH}-\text{CH}_2 \end{array}\right]_n$	poly(propenenitrile)	Polyacrylonitrile acrylic fibre COURTELLE	clothing
$\text{CF}_2=\text{CF}_2$	$-\text{CF}_2-\left[\text{CF}_2\right]_n$	Poly(1,1,2,2-tetrafluoroethene)	TEFLON	Coating cookware (non-stick)