

Alkenes

Alkenes are a family of hydrocarbons (compounds containing carbon and hydrogen only) containing a carbon-carbon double bond. The first two are:

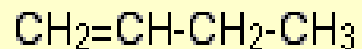
ethene C_2H_4
propene C_3H_6

You can work out the formula of any of them using: C_nH_{2n} .

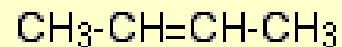
Isomerism in the alkenes

Structural isomerism: All the alkenes with 4 or more carbon atoms in them show structural isomerism. This means that there are two or more different structural formulae that you can draw for each molecular formula.

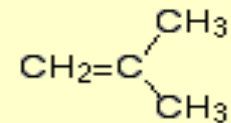
For example, with C_4H_8 , it isn't too difficult to come up with these three structural isomers:



but-1-ene



but-2-ene



2-methylpropene

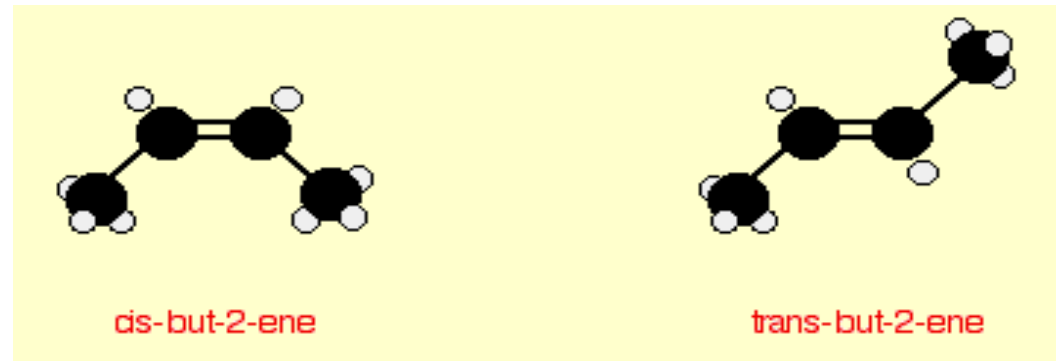
Alkenes

In fact for but-2-ene there is another isomer. A geometrical isomer.

Geometric (cis-trans) isomerism

The carbon-carbon double bond doesn't allow any rotation about it. That means that it is possible to have the CH₃ groups on either end of the molecule locked either on one side of the molecule or opposite each other.

These are called cis-but-2-ene (where the groups are on the same side) or trans-but-2-ene (where they are on opposite sides).

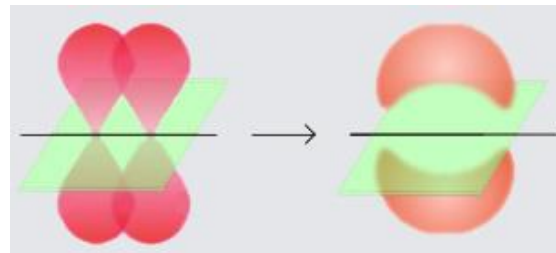


Alkenes

The shape of alkenes

Ethene is a flat molecule. The geometry around each carbon atom is based on a trigonal planar shape, because each carbon has three electrons around it. This should make the angle of each bond 120. However, the H-C bond angles are in fact 118, because the four electrons in the carbon-carbon double bond repel more than the pair of electrons in the carbon-hydrogen single bonds.

Unlike the C-C bonds in alkanes there is no rotation about the double bond. This is caused by the bonding orbitals that take part in the double bond, the sigma bond (caused by end to end overlap of the p orbitals) and the pi bond (caused by overlap of p orbitals above and below the sigma bond).



Alkenes

Physical properties of the alkenes

Boiling Points

The boiling point of each alkene is very similar to that of the alkane with the same number of carbon atoms. Ethene, propene and the various butenes are gases at room temperature. All the rest that you are likely to come across are liquids.

In each case, the alkene has a boiling point which is a small number of degrees lower than the corresponding alkane. The only attractions involved are Van der Waals dispersion forces, and these depend on the shape of the molecule and the number of electrons it contains. Each alkene has 2 fewer electrons than the alkane with the same number of carbons.

Solubility

Alkenes are virtually insoluble in water, but dissolve in organic solvents.

Alkenes

How alkenes react

The double bond makes a huge difference to the reactivity of alkenes when compared with alkanes. The bond energy for a C-C bond is 347 kJ mol^{-1} and 612 kJ mol^{-1} for C=C bonds, so you would automatically predict that alkenes would be less reactive than alkanes but this is not true.

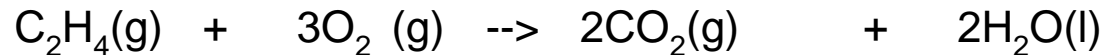
- Firstly a double bond is made up of two parts, a π and σ bond. The σ bond is the same as the alkane therefore a π bond must have an energy of $612 - 347$ which gives us 265 kJ mol^{-1} . So it is in fact quite easy to break the π part of the double bond, and this is exactly what happens in most alkene reactions.
- Secondly when this does happen it leaves carbon atoms needing new bonds, so new groups can be added on.
- Thirdly due to the high number of electrons involved in a double bond, the area is very electron rich. This makes it a very susceptible to electrophilic attack.

So as you should already know, most of the reactions of alkenes are electrophilic additions.

Reactions of Alkenes

Combustion

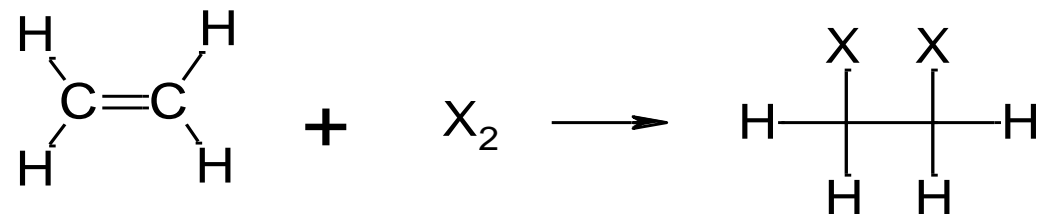
Alkenes can burn in air:



Though they burn in air, we do not use them as fuels because they are far too important to waste them this way.

Reactions of alkenes with halogens (electrophilic addition).

Alkenes react rapidly with chlorine gas, or with solutions of bromine and iodine in an organic solvent, to give 1,2-dihalogenalkanes.



Where X_2 is any halogen molecule. The halogen atoms add across the double bond.

Reactions of Alkenes

The test for a double bond

The addition reaction is used to test for a carbon-carbon double bond. When a few drops of bromine solution (reddish brown) is added to an alkene the solution is decolourised because halogenalkanes are formed and are colourless.

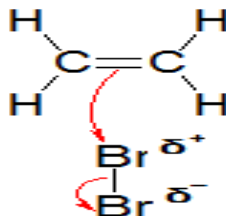
The mechanism

The mechanism by which bromine reacts is a typical electrophilic addition.

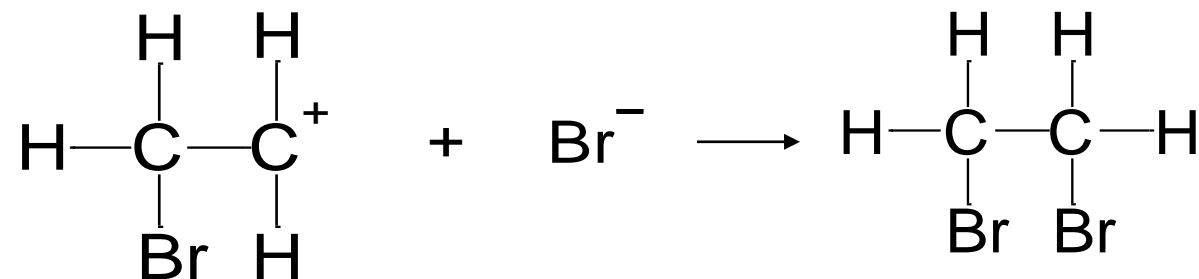
● The electrophile attacks. At any instant a bromine molecule is likely to have an instantaneous dipole $\text{Br}^{\delta+} - \text{Br}^{\delta-}$. (An instant later that dipole could be reversed.) The $\delta+$ end of this dipole is attracted to the electron rich double bond in the alkene – it is an electrophile.

● 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 this strengthens the dipole of the bromine molecule.

Reactions of Alkenes



● A positive ion (a carbocation) is formed. Two electrons from the double bond form a bond with the Br δ⁺ and the other bromine atom becomes a Br⁻ ion. This leaves the carbocation, in which the carbon atom that is not bonded to the bromine has a positive charge.



● A negative ion bonds to the carbon that has the positive charge. The carbocation is rapidly attacked by any negative ion. The only negative ion present in a non-aqueous solution will be the Br⁻.

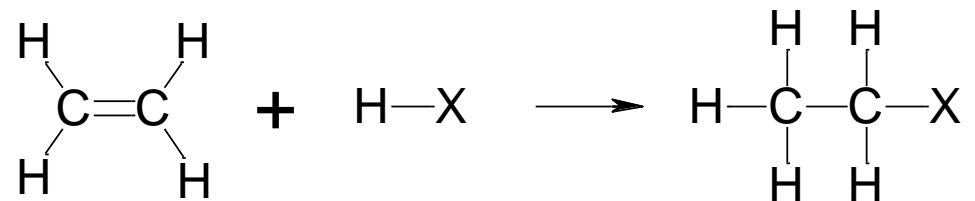
● So the addition takes place in two steps:

1. Formation of the carbocation by electrophilic addition
2. Rapid reaction with a negative ion.

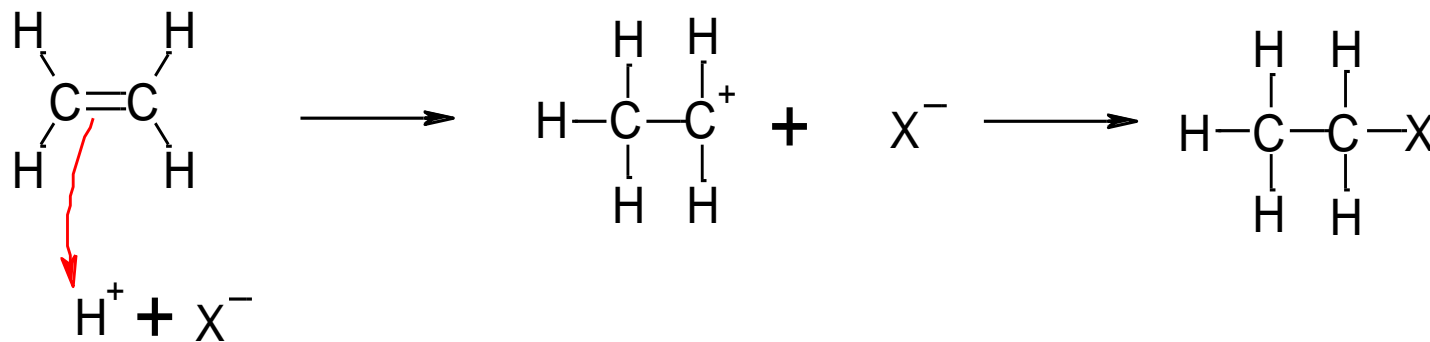
Reactions of Alkenes

Reactions with hydrogen halides

Hydrogen halides, HCl, HBr and HI add across a double bond to form halogenoalkanes.

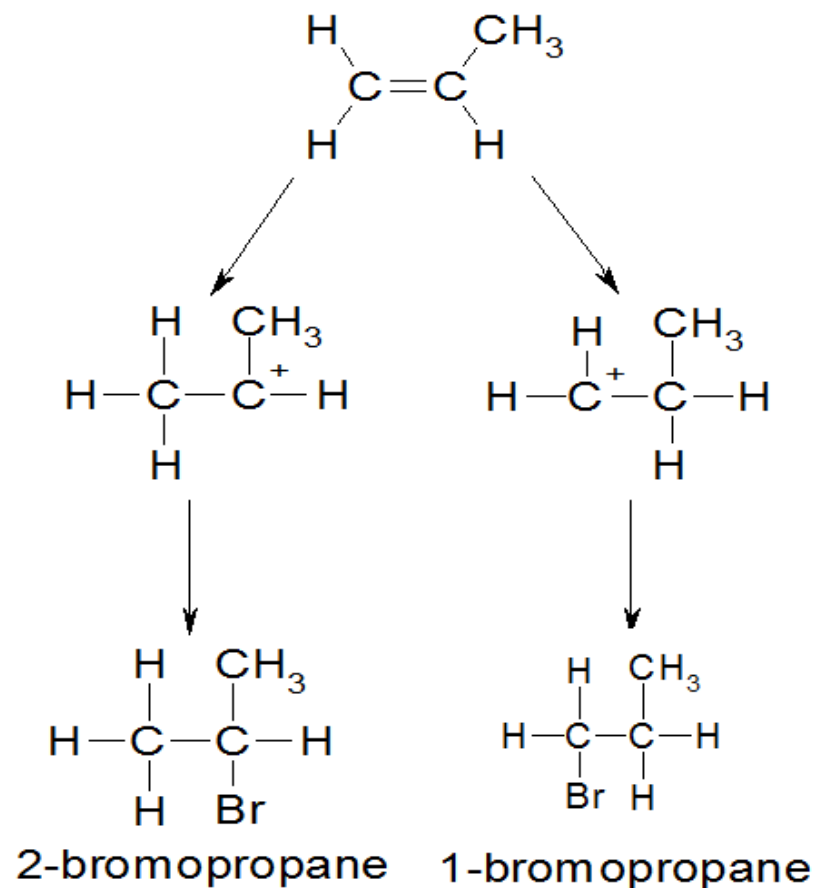


The H-X bond breaks heterolytically to give H⁺ X⁻. The H⁺ ion is a good electrophile and forms a bond with the two electrons in the double bond. This leaves a positively charged ion (C⁺) that is then rapidly attacked by the X⁻ ion.



Reactions with Alkenes

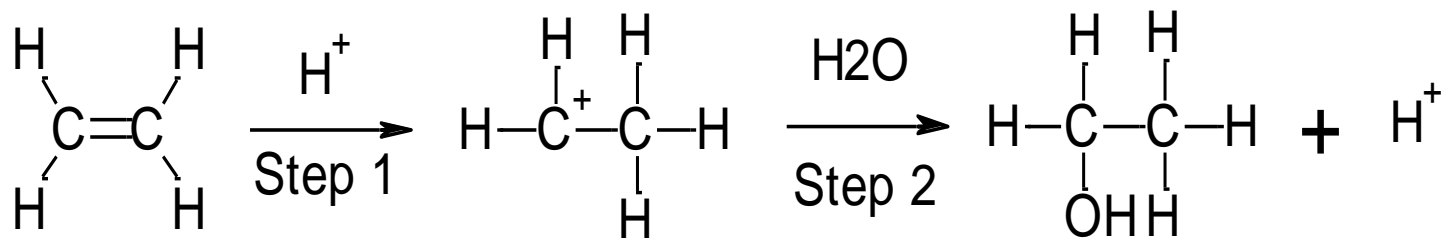
With the previous mechanism we used ethene. Because the double bond is in the middle of the carbon chain we can only get one possible product. If the double bond is not in the middle of the chain then there are two possible products because the hydrogen halide can bond to either of the carbon atoms of the double bond.



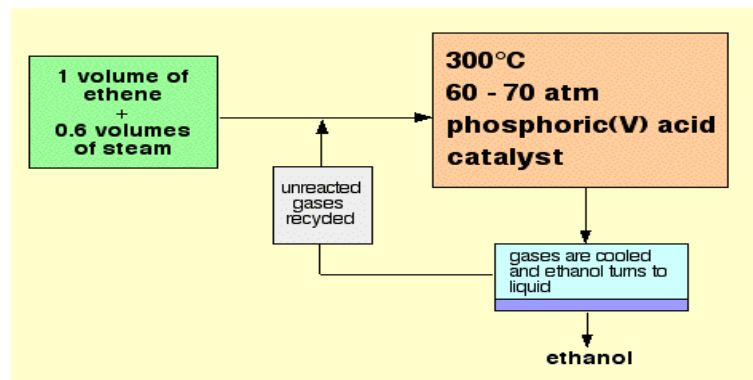
NB: This is not entirely true. The major product in this reaction is 2-bromopropane, and is due to Markovnikov's rule which says: "When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already." **(Be aware that for the exam you do NOT need to know this).**

Reactions of Alkenes

Water also adds across a double bond in alkenes, and is used industrially to make alcohols and is carried out with steam and an acid catalyst such as phosphoric acid (H_3PO_4). Notice how the H^+ ion which comes from the acid catalyst is used in step 1, but reformed in step 2, hence acting as a catalyst.



The one example you must know in full, including reaction conditions is for the production of ethanol from ethene.



Reactions of Alkenes

Hydrogen reacts with alkenes by adding across the double bonds to make them into alkanes. This takes place using a highly porous nickel catalyst called Raney Nickel at room temperature and pressure.



This is a fairly pointless reaction because ethene is a far more useful compound than ethane!

Margarine manufacture

Some margarine is made by hydrogenating carbon-carbon double bonds in animal or vegetable fats and oils. You can recognise the presence of this in foods because the ingredients list will include words showing that it contains "hydrogenated vegetable oils" or "hydrogenated fats".

The reason they do this is to increase the hardness of the fat or oil. Less double bonds cause the melting point to increase because the molecules are now more regularly shaped and pack together better. In industry the reaction is carried out at around 420K and 500 kPa using the a powered nickel catalyst. The reaction is controlled so that only enough double bonds are removed to gain the correct hardness, because Unsaturated fats actually have dietary advantages over saturated ones.