

THE REACTIONS OF ALKENES

This page looks at the reaction of the carbon-carbon double bond in alkenes such as ethene with halogens such as chlorine, bromine and iodine. This is called halogenation.

Simple reactions involving halogens

In each case, we will look at ethene as typical of all of the alkenes. There are no complications as far as the basic facts are concerned as the alkenes get bigger.

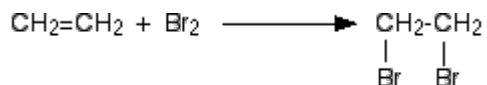
Ethene and fluorine

Ethene reacts explosively with fluorine to give carbon and hydrogen fluoride gas. This isn't a useful reaction, and you aren't likely to need it for exam purposes in the UK at this level (A level or equivalent).



Ethene and chlorine or bromine or iodine

In each case you get an *addition reaction*. For example, bromine adds to give 1,2-dibromoethane.

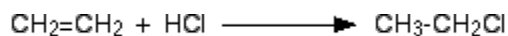


Addition to symmetrical alkenes

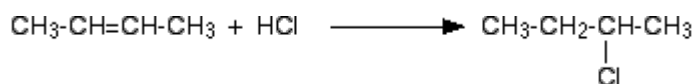
What happens?

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other.

For example, with ethene and hydrogen chloride, you get chloroethane:



With but-2-ene you get 2-chlorobutane:



Reaction rates

1. Variation of rates when you change the halogen

Reaction rates increase in the order $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

Hydrogen fluoride reacts much more slowly than the other three. Why?

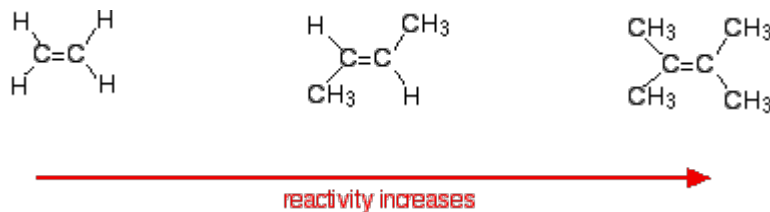
- When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken.
- The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong.
- Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

2. Variation of rates when you change the alkene

This applies to unsymmetrical alkenes as well as to symmetrical ones.

Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond. Why?

For example:



There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Reaction Mechanisms

It is due to two reasons

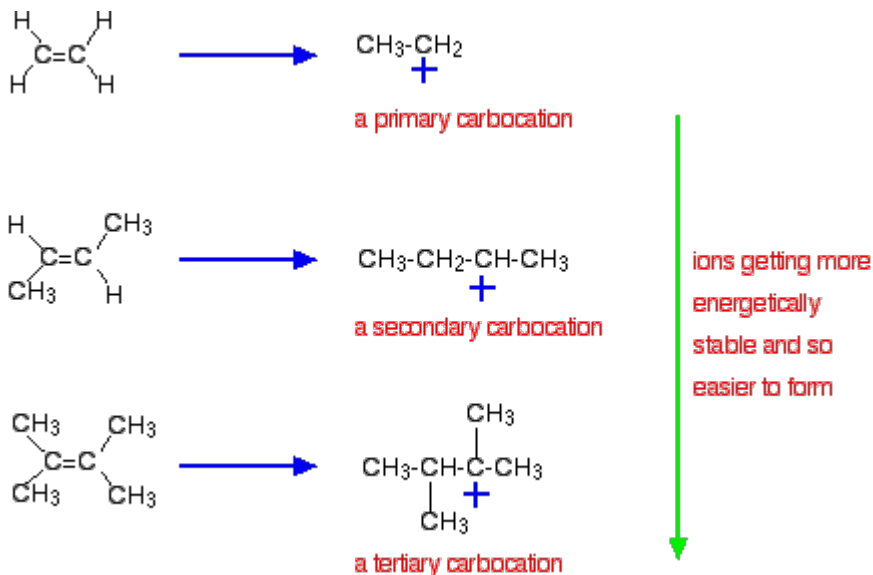
A) Inductive effect

- Alkenes react because **the electrons in the pi bond attract things with any degree of positive charge.**
- Anything which **increases the electron density around the double bond** will help this.
- **Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. (Inductive effect)**
- The more alkyl groups you have, the **more negative the area around the double bonds becomes.**
- The **more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride.**

2. Stability of the carbocation

The more important reason, lies in the stability of the intermediate ion formed during the reaction.

The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



- The stability of the intermediate ions governs the activation energy for the reaction.
- As you go towards the more complicated alkenes, the activation energy for the reaction falls.
- That means that the reactions become faster.

Addition to unsymmetrical alkenes

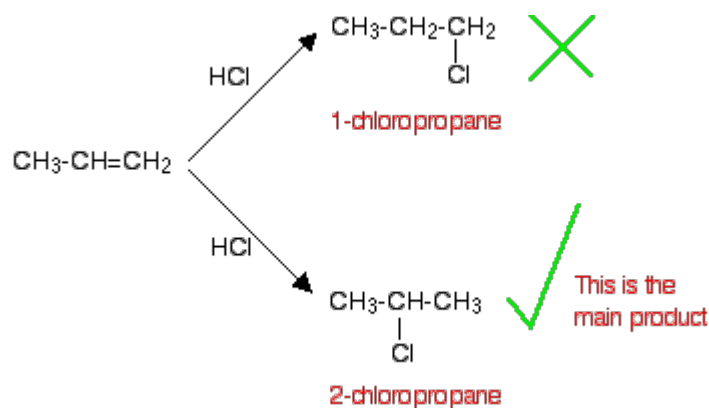
What happens?

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above.

The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond.

Orientation of addition

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.



This is in line with *Markovnikov's Rule* which says:

When a **compound HX is added to an unsymmetrical alkene**, the **hydrogen gets attached to the carbon with the most hydrogens attached to it already**.

- In this case, the hydrogen becomes attached to the CH_2 group, because the CH_2 group has more hydrogens than the CH group.
- Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the CH_3 group are totally irrelevant.

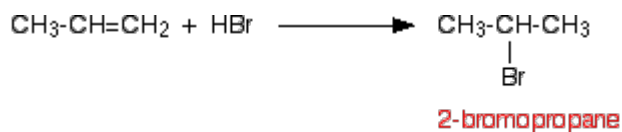
A special problem with hydrogen bromide

Unlike the other hydrogen halides, hydrogen bromide can add to a carbon-carbon double bond *either* way around - depending on the conditions of the reaction.

1. If the hydrogen bromide and alkene are entirely pure

In this case, the **hydrogen bromide adds on** according to **Markovnikov's Rule**.

For example, with propene you would get 2-bromopropane.



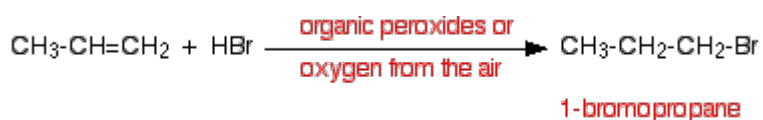
That is exactly the same way that other hydrogen halides add.

2. If the hydrogen bromide and alkene contain traces of organic peroxides (*anti-Markovnikov addition* /the *peroxide effect*.)

Oxygen from the air tends to react slowly with alkenes to produce some organic peroxides, (you don't necessarily have to add them separately).

This the reaction that that would take place unless all the precautions are taken to exclude all air from the system.

In this case, the addition is the other way around, and you get 1-bromopropane:



This is sometimes described as an *anti-Markovnikov addition* or *peroxide effect*.

- Organic peroxides are excellent sources of free radicals.
- In the presence of these, the hydrogen bromide reacts with alkenes using a different (faster) mechanism.
- For various reasons, this doesn't happen with the other hydrogen halides.
- This reaction can also happen in the presence of ultra-violet light
- The right wavelength to break the hydrogen-bromine bond into hydrogen and bromine free radicals.

ALKENES and POTASSIUM MANGANATE(VII)

Oxidation of alkenes with cold dilute potassium manganate(VII) solution

Experimental details

Alkenes react with potassium manganate(VII) solution in the cold.

A) If the potassium manganate(VII) solution (acidified with dil. H_2SO_4) + Alkene

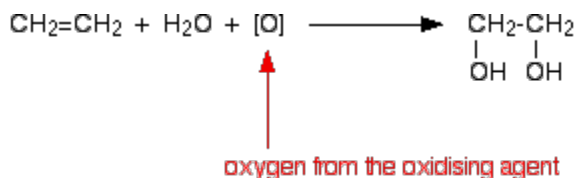
(purple solution) → (colourless).

B) If the potassium manganate(VII) solution alkaline (slightly alkaline sodium carbonate solution)

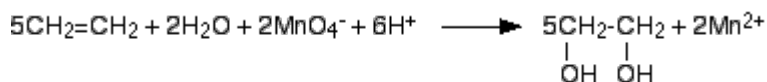
(purple solution) → dark green solution → dark brown ppt

Chemistry of the reaction

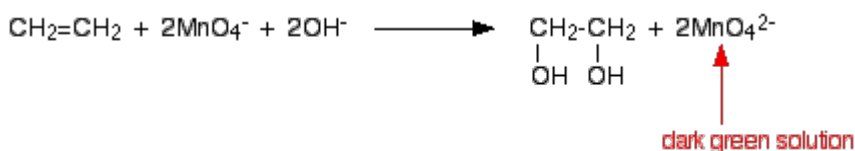
- Manganate(VII) ions are a strong oxidising agents, oxidise ethene → ethane-1,2-diol



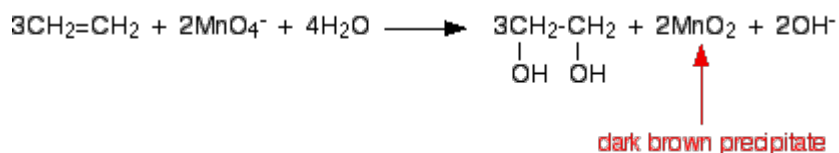
1. Under acidic conditions, the manganate(VII) ions are reduced to manganese(II) ions.



Under alkaline conditions, the manganate(VII) ions are first reduced to green manganate(VI) ions



but eventually you get dark brown solid manganese(IV) oxide (manganese dioxide) formed. The overall equation for the formation of this from the manganate(VII) ions is:



Using the reaction to test for carbon-carbon double bonds

Not a good test to see if double bonds are there. It may be an indicator of presence of double bonds. But there are many other compounds that could give that same observation with Permanganate(VII) solution(cold/alkaline). Acidic/Permanganate solution will be too reactive and break the C=C before the reaction, therefore it is rarely used in organic chemistry.

Alkaline potassium manganate(VII) solution can be used only if there is a mixture of an alkane or an alkene – (when there is nothing else present which could be oxidized).

UNIT 2 /A2 Level

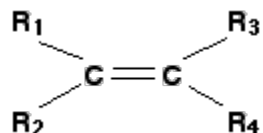
Oxidation of alkenes with hot concentrated acidified potassium manganate(VII) solution

- In the presence of Hot conc acid the reaction won't stop after making the di-ol.

- Di-ol could be quite easily further oxidized by manganate(VII) ions.
- That means that the reaction won't stop unless *very* dilute, very cold, and preferably not under acidic conditions.

In the presence of hot concentrated acidified potassium manganate(VII) solution, final products depends on the arrangement of groups around the carbon-carbon double bond.

If you represent a simple alkene: Where R1 R2 R3, R4 are alkyl gps

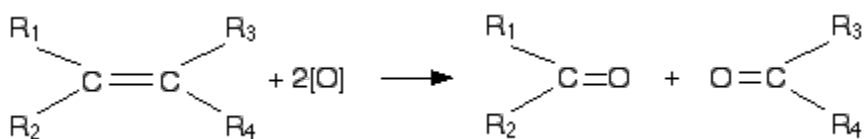


The first stage of the extended oxidation

The acidified potassium manganate(VII) solution break the carbon-carbon double bond oxidizes

alkene \rightarrow 2 Carbonyl compounds

(two carbon-oxygen double bonds; C=O.)

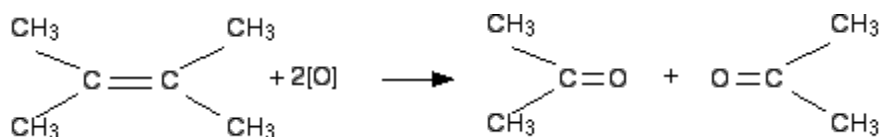


how they react depends on what gps are attached to the carbon-oxygen double bond.

A) If both attached R groups in the products are alkyl groups

- If two alkyl gps are attached to the both side of the double bond \rightarrow Ketones. Ketones aren't that easy to oxidize, and so there is no further action.
- If the alkyl groups attached to either side of the original carbon-carbon double bond were the same, then you would end up with a single ketone.
- If they were different, then you would end up with a mixture of two ketones.

Example: 1.



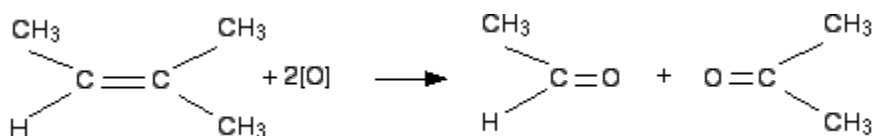
- two identical Ketones propanone is formed.

Example 2-R₁, R₃,R₄- methyl group R₂= Ethyl gp, a mixture of two different ketones(propanone and butanone) are formed

Example 3 – R₁, R₃ – Methyl and R₂ and R₄ ethyl- a single ketone formed (1-butanone) is formed.

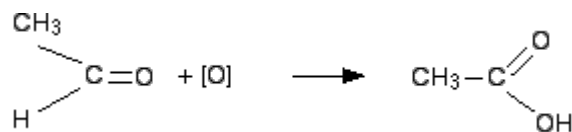
Example 4- If a product has one hydrocarbon group and one hydrogen

For example, suppose the first stage of the reaction was:

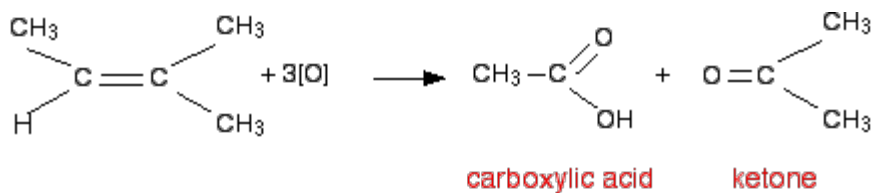


first product - has a methyl group and a "hydrogen" attached to the carbonyl group → aldehyde.

Aldehydes are readily oxidized-→ (to give carboxylic acids, containing the -COOH group). Ethanoic acid, CH₃COOH.



The overall effect of the potassium manganate(VII) on this kind of alkene is therefore:

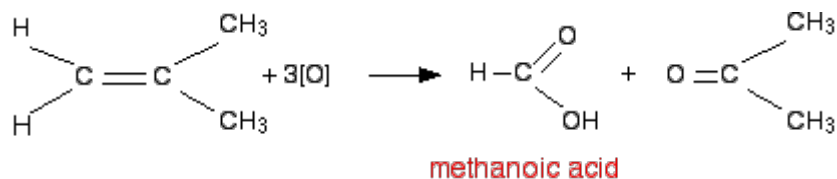


- if there was a hydrogen atom attached to both carbons at the ends of the carbon-carbon double bond →, two carboxylic acid molecules are formed

- which might be the same or different, depending on whether the alkyl groups were the same or different.

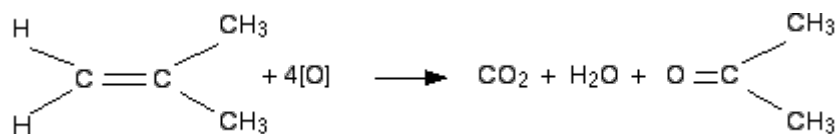
If a product has two hydrogens but no hydrocarbon group

You may expect methanoic acid to be one of the the final products,



But methanoic acid \rightarrow easily oxidised / potassium manganate(VII) \rightarrow CO_2 and H_2O carbon dioxide and water.

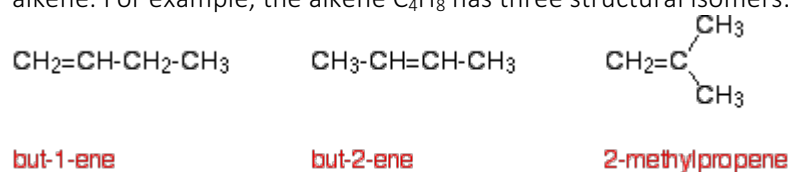
So the equation in a case like this might be, for example:



The exact nature of the other product (in this example, propanone) will vary depending on what was attached to the right-hand carbon in the carbon-carbon double bond.

If you reacted ethene \rightarrow only products CO_2 and H_2O

Working back from the results helps you to work out the structure of the alkene. For example, the alkene C_4H_8 has three structural isomers:



- Isomer A gives a ketone (propanone) and carbon dioxide.
- Isomer B gives a carboxylic acid (propanoic acid) and carbon dioxide.
- Isomer C gives a carboxylic acid (ethanoic acid).
- Identify Isomer A, B and C