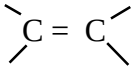
ALKENES

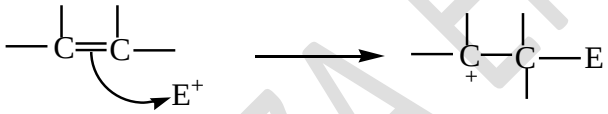
They have a general formula of $C_n H_{2n}$. The functional group is the carbon to carbon double bond i.e.



They are called unsaturated hydrocarbons because the double bond can open to allow alkenes take up more hydrogen atoms or other species forming saturated products.
The aliphatic non-cyclic alkenes have a general molecular formula of C_nH_{2n}.
The unsaturated carbon atoms are sp^2 hybridized. They are attached to each other by a:

- sigma (σ) bond from the sp^2 hybrid, resulting from the sharing of a pair of electrons between the two carbon atoms due to the overlapping of two of the hybrid orbitals (i.e. one from each carbon atom).
- pi (π) bond which is formed between the two carbon atoms due to the overlapping of the non-hybridized p-orbitals (unshared electrons in the p-orbitals of the carbon atoms). The pi bond lies at right angles to the plane of the hybrid orbitals and is localized between the two carbon atoms.

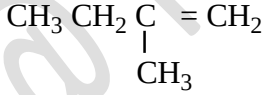
The remaining sp^2 hybrid orbitals form sigma bonds with other carbon or hydrogen atoms. In alkenes, the pi bond electrons are more exposed than the sigma bond electrons and therefore are more available hence vulnerable to any attacking species, particularly electrophiles. This availability of electrons makes alkenes to be more reactive than alkanes.
When the electrophile attacks an alkene, the available pi bond electrons are converted into a new sigma bond between an atom of the attacking species and one of the carbon atoms from the double bond. Hence the electrophile being added to the unsaturated alkene to form a saturated product.



Isomerism

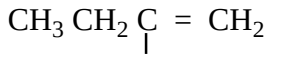
1) **Chain isomerism.** Here the position of the double bond does not change but they form straight chains and branched chains. e.g. Molecular formula $C_5 H_{10}$

(straight chain isomer)

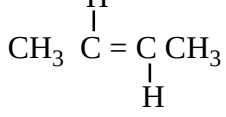


(branched chain isomer)

2) **Position isomerism.** This is where the position of the double bond changes.
e.g. C_4H_8



(double bond at position 1)

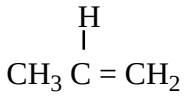


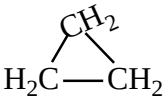
(double bond at position 2)

3) **Geometric isomerism.** It consists of both the cis and trans isomers.

4) **Ring isomerism / functional group isomers**

Alkenes and cyclo alkanes are isomeric. The hydrocarbons have carbon atoms arranged in a ring for cycloalkanes while in alkenes they are not. e.g. C_3H_6

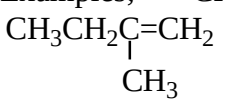




Nomenclature

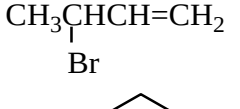
- First consider the double bond when naming. The carbon atoms are numbered from the end closest to the double bond.
- The position of the double bond is indicated using the number of carbon atom preceding the double bond.
- When both a halogen group and a double bond are present in a compound, the double bond takes precedence in the naming of the compound. The carbon chain is therefore numbered in such a way that the position of the double bond is lower than that of the halogen.

Examples; $CH_3CH=CH_2$ propene $CH_3\,CH_2\,CH = CH_2$ but-1-ene

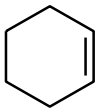


2-methylbut-1-ene

$CH_3CH=CHCH_3$ but–2–ene

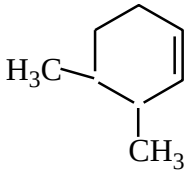


3-bromobut-1-ene

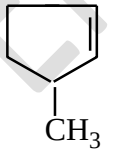


Cyclohexene

Cyclopentene



3,4-dimethylcyclohexene



3-methylcyclopentene

Physical Properties of Alkenes

- They are insoluble in water.
- They have a lower density than in water.
- They have lower but very close melting points and boiling points as compared to the corresponding alkanes.

Preparation of Alkenes

1) **Industrial preparation of alkenes.** They are prepared by cracking of petroleum or larger alkanes. The alkanes. The alkane or petroleum vapour is passed over heated catalyst. e.g.

$$C_9\,H_{20} \xrightarrow[SiO_2/Al_2O_3]{450^oC} C_2\,H_4 + C_7H_{16}$$

2) **Laboratory preparation of alkenes**

(a) **Dehydration of alcohols**

(i) By reaction of alcohols in the liquid phase with hot and concentrated sulphuric acid or phosphoric acid.

In this reaction, there's loss of a water molecule due to presence of dehydrating agents.

Water being a neutral nucleophile and is a product of this reaction, the mechanism followed is hence referred to as a *nucleophilic elimination* reaction mechanism. i.e.

$$RCH_2CH_2OH \xrightarrow[\text{heat (170 - 180}^oC)]{\text{Conc } H_2SO_4 \text{ or } H_3PO_4} RCH = CH_2 + H_2O$$

where R is an alkyl, aryl (phenyl) or cyclo group.

The ease of dehydration depends on the nature or class of the alcohol (i.e. the ease with which the reaction takes place).

The reaction is occurs most easily with a tertiary alcohol, followed by a secondary alcohol and least easily with the primary alcohol.

In order to know the class of the alcohol, one determines the number of carbon atoms to which the carbon atom with the functional group is bonded. (i.e. for tertiary, the carbon atom with the functional group is bonded to 3 other carbon atoms, secondary with 2 carbon atoms and primary with 1 carbon atom).

Note:

i) Since secondary and tertiary alcohols can easily be dehydrated, a lower concentration of the acid and a lower temperature may be used. i.e.

for a secondary alcohol, 60% conc. H_2SO_4 and a temperature as low as 120^{o}C may be used.

for a tertiary alcohol, 20% conc. H_2SO_4 and a temperature as low as 85^{o}C may be used.

ii) With phenyl or cyclo alcohols, concentrated phosphoric acid is preferably used. The reaction may also take place with minimal heating.

Some examples of alcohols being dehydrated to form alkenes include:

- for a primary alcohol like ethanol

$$CH_3\,CH_2\,OH \xrightarrow[170\ -\ 180^oC]{\text{Conc } H_2SO_4} CH_2 = CH_2 + H_2O$$

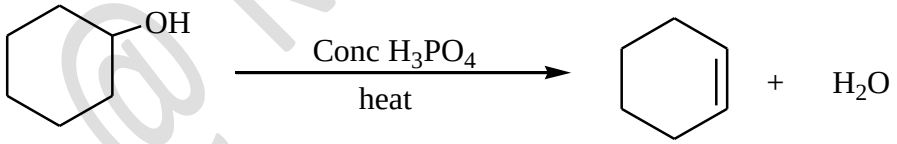
- for a secondary alcohol like propan-2-ol

$$CH_3\,\underset{\displaystyle OH}{\underset{|}{CH}}\,CH_3 \xrightarrow[170 - 180^oC \text{ or heat}]{\text{Conc } H_2SO_4} CH_3\,CH = CH_2 + H_2O$$

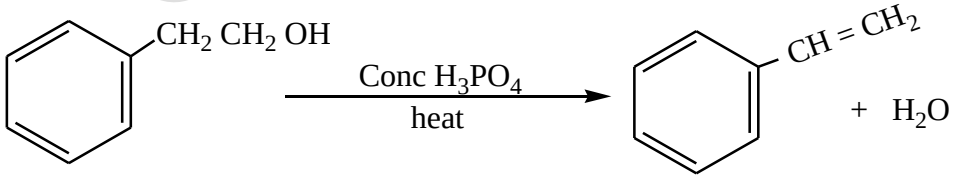
- for a tertiary alcohol like 2-methylpropan-2-ol

$$CH_3\,\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}\,-\,CH_3 \xrightarrow[170 - 180^oC \text{ or heat}]{\text{conc } H_2SO_4} CH_3\,\underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2 + H_2O$$

- for a cyclo alcohol like cyclohexanol



- for a phenyl alcohol like 2-phenylethanol



e.t.c

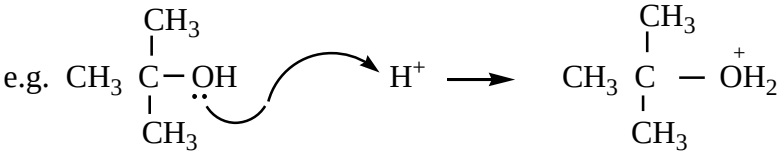
Mechanism of the reaction:

The reaction mechanism generally involves 3 stages (steps) for all classes of alcohols.

Step 1 - Protonation of the hydroxyl group of the alcohol:
The alcohol has 2 lone pairs of electrons on the oxygen atom of the hydroxyl group hence being a nucleophile. One of the lone pairs of electrons on the oxygen atom is attacked by a proton (an electrophile) from the acid. The alcohol is converted to a protonated alcohol.

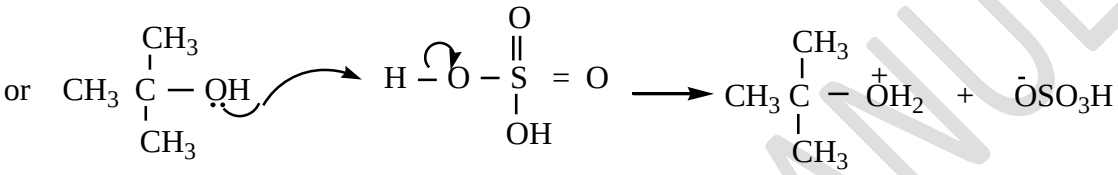
$$H_2SO_{4(aq)} \rightleftharpoons H^+_{(aq)} + HSO^-_4 \text{ (or } {}^-OSO_3H)$$

e.g.

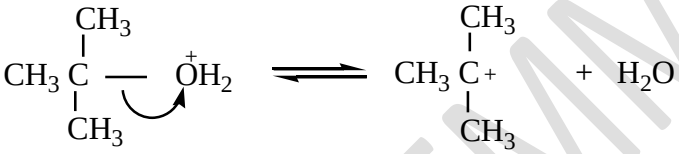


(tertiary alcohol) (protonated tertiary alcohol)

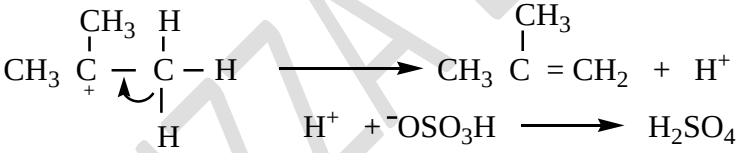
or



Step 2 - Loss of a water molecule to form a carbo cation. This is because, the hydroxyl group was converted into a good leaving water group.

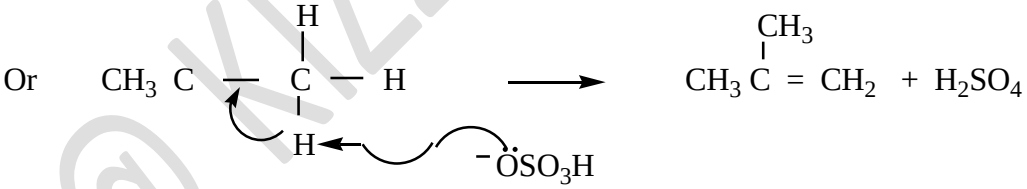


Step 3 – Loss of a proton from the carbocation. The carbocation is very unstable hence rapidly loses a proton to form a stable neutral molecule. The proton is lost from a carbon atom next to one with the positive charge. i.e.



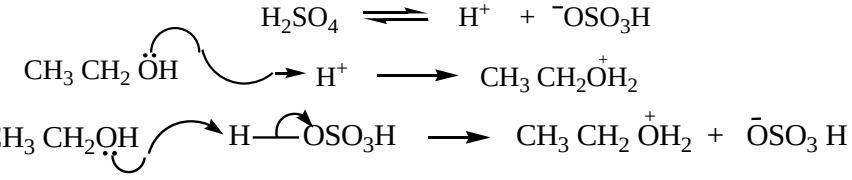
$$H^+ + {}^-OSO_3H \longrightarrow H_2SO_4$$

Or

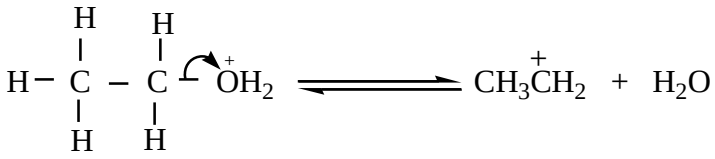


For a **primary alcohol, it involves:**
Step 1: Protonation of the hydroxyl group
e.g.

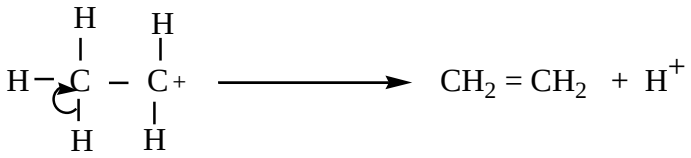
$$H_2SO_4 \rightleftharpoons H^+ + {}^-OSO_3H$$

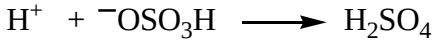


Step 2: Loss of a water molecule

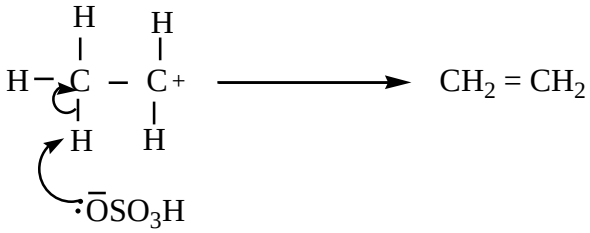


Step 3: Loss of a proton.

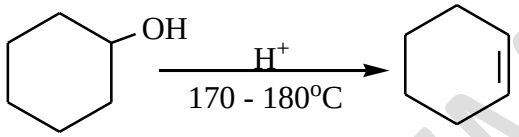




or

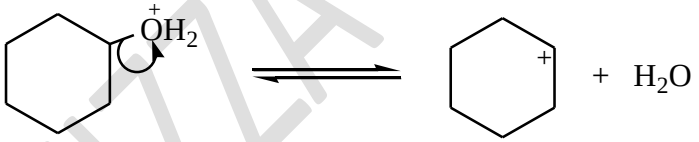


For a **secondary alcohol.** e.g.



Step 1

Step 2



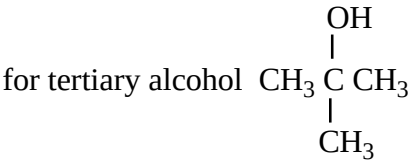
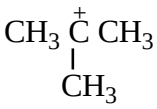
Step 3

Note that:

There are 3 types of carbo cations that can be formed during the mechanism by the 3 classes of alcohols (primary, secondary and tertiary). e.g.

for primary alcohols $CH_3\,CH_2\,CH_2\,CH_2OH$ form primary carbocations $CH_3\,CH_2CH_2\overset{+}{C}H_2$

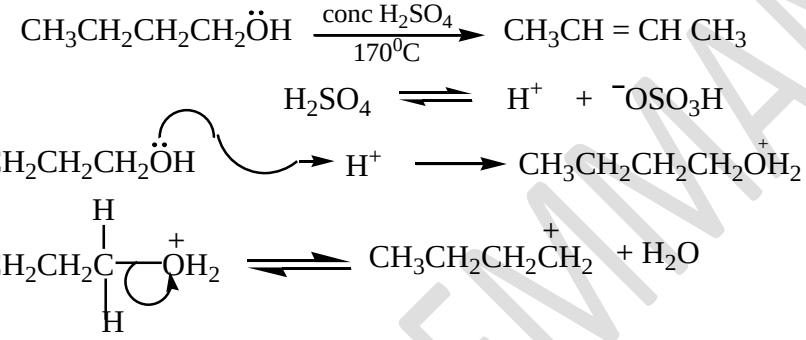
for secondary alcohols $CH_3\,CH_2\overset{OH}{\overset{|}{C}}HCH_3$ form secondary carbo cations $CH_3\,CH_2\overset{+}{C}HCH_3$

for tertiary alcohol  form tertiary carbo cations 

Because all alkyl groups are electron releasing groups (have positive inductive effect), the positive charge on the tertiary carbo cation is highly neutralized and this makes it the most stable followed by the secondary and the primary is the least stable.

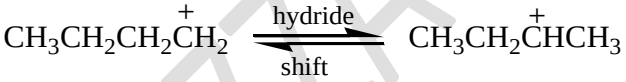
Note that the tertiary carbo cation has 3 alkyl groups, the secondary has two alkyl groups while the primary has one alkyl group.

Hence in dehydration of a straight chain primary alcohol with 4 or more carbon atoms along the parent chain, two carbocations and hence two products may be formed (A major product and a minor product). e.g. **dehydration of butan-1-ol** yields but-2-ene as the major product (95%) while but-1-ene is the minor product (5%). Thus the main product from the reaction is but-2-ene but not but-1-ene as expected. i.e.

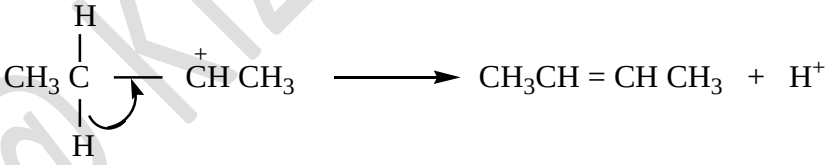


The primary carbocation formed is very unstable and hence undergoes rearrangement by *hydride shift* to form a more stable secondary carbo cation before proton loss takes place.

(A small fraction of about 5% of the primary carbocation is converted into but-1-ene)

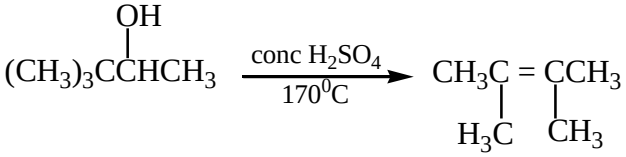


The reaction preferably proceeds via the more stable secondary carbo cation to produce but-2-ene.

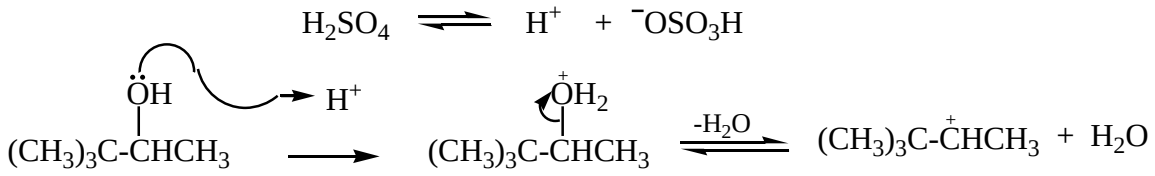


This explains why dehydration of butan-1-ol, yields but-2-ene as the product and not but-1-ene.

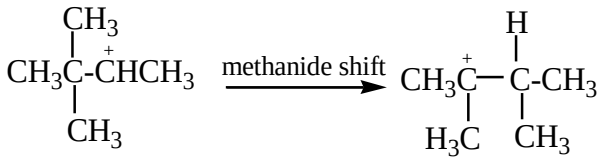
Similarly dehydration of 2,2-dimethylbutan-2-ol yields 2,3-dimethylbut-2-ene as the major product while 2,3-dimethylbut-1-ene is the minor product.

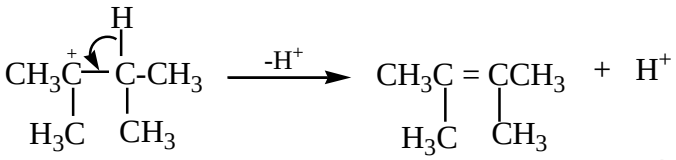


Mechanism:



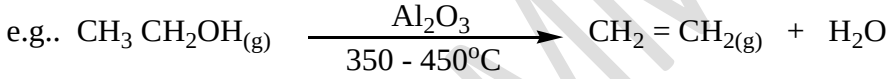
The secondary carbocation formed is less stable and hence undergoes rearrangement by *methanide (methyl) shift* to form a more stable tertiary carbo cation before proton loss takes place to form the major product.





then

ii) By reaction of alcohols in the vapour phase overheated aluminium (III) oxide as a catalyst. This reaction is suitable in preparation of gaseous alkenes from gaseous alcohols. porcelain or pumise stones can also be used as catalysts.



(b) **By reaction of halogeno alkanes** (aliphatic, cyclic or aromatic) **with a hot and concentrated alcoholic alkali solution.** i.e. The halogeno alkane is boiled or refluxed with aqueous KOH or NaOH in presence of ethanol.

Dehydrohalogenation of the halogeno alkane takes place giving rise to an alkene. Since a hydrogen and a halogen atom are lost from a saturated compound leading to formation of an unsaturated product (alkene), the reaction is refered to as an *elimination reaction.*

This reaction takes place most easily with tertiary halogeno alkanes followed by secondary halogeno alkanes. It's because during the reaction, tertiary halogeno alkanes form the most stable carbocations, hence react fastest followed by secondary halogeno alkanes.

The reaction with primary halogeno alkanes is very slow and thus they form an ether as the major organic product through a *substitution reaction* and about 2% of the alkene.

Therefore, the ratio of ***elimination is favoured*** to substitution when:

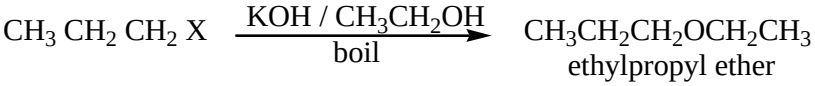
- the solvent is changed from water to an alcohol.
- sodium or potassium hydroxide solution is concentrated.
- the temperature is increased.

- the number of alkyl groups adjacent to the carbon atom with the halogen are increased. i.e. tertiary and secondary halogeno alkanes are favoured.

Type of halogenoalkane	*Substitution or elimination?*
Primary	mainly substitution
Secondary	slightly substitution but mainly elimination
Tertiary	mainly elimination

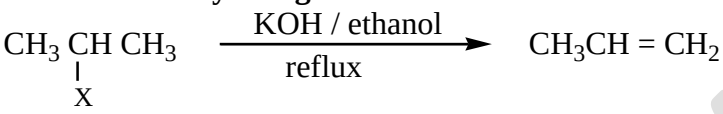
Examples:

- for a primary halogeno alkane

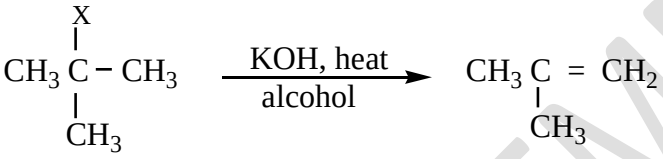


where X is a halogen Cl, Br or I.

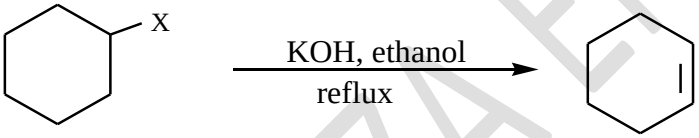
- for a secondary halogeno alkane



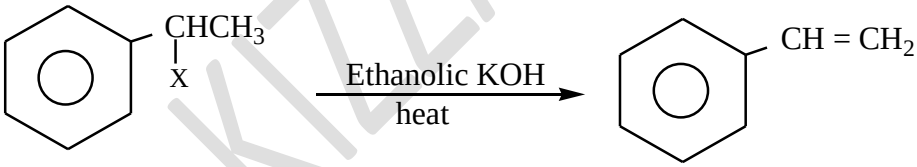
- for a tertiary halogeno alkane



- for a cyclic halogeno alkane



- for an aromatic halogeno alkanes

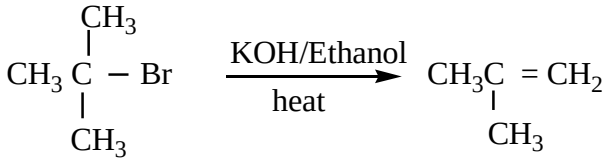


etc

Note: The reagent ethanol can be represented as EtOH. Et is an abbreviation for an Ethyl group. This reaction is regarded as an **elimination** reaction because the halogeno alkane loses both hydrogen and halogen atoms.

Mechanism of the reaction:

For a tertiary halogeno alkane, the elimination reaction mechanism involves 2 main steps. e.g. 2-bromo-2-methyl propane



Before elimination, the alcohol reacts with the base to form a salt containing an alkoxide ion from an alcohol, (e.g. ethoxide from ethanol) that acts as a stronger base.

$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$

then $CH_3CH(OH) + OH^- \longrightarrow CH_3CH_2O^- + H_2O$

(ethoxide ion)

Or $KOH + CH_3CH_2OH \longrightarrow CH_3CH_2O^-K^+ + H_2O$

then $CH_3CH_2O^-K^+ \longrightarrow CH_3CH_2O^- + K^+$

Step 1:

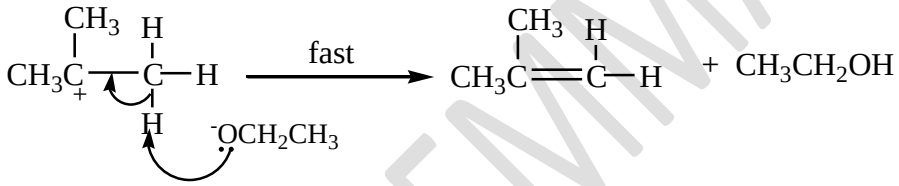
Ionisation of the tertiary halogeno alkane. This is due to steric hindrance (restraining of a reaction process from taking place due to the presence of crowded large bulk groups around an organic reaction site).

$(CH_3)_3C{-}Br \underset{}{\overset{\text{slow}}{\rightleftharpoons}} (CH_3)_3C^+ + Br^-$

This is a slow process because it involves breaking a bond where energy is required. It's a reversible process because the ions formed can recombine to regenerate the halogeno alkane.

Step 2:

The ethoxide (alkoxide) ion accepts a proton from the hydrogen atom of the carbon atom adjacent to the positively charged carbon (i.e. the $CH_3CH_2O^-$ abstracts a hydrogen atom in form of a proton from the carbon atom next to the one carrying a positive charge).



Ethanol is regenerated since it acts as a catalyst. The Br^- in step 1 contains with K^+ to form KBr.

$K^+ + Br^- \longrightarrow KBr$

The above mechanism is regarded as **elimination unimolecular (E_1) reaction mechanism** because only one specie (particle or molecule) was involved in the rate determining step. This is the slow step where the bond between the carbon atom and the functional group is being broken. This step therefore determines the rate of the reaction.

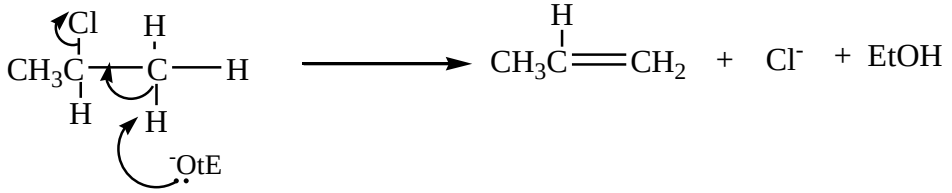
For a secondary halogeno alkane, two steps (for **elimination unimolecular mechanism**) or one step (for **elimination bimolecular mechanism**) may be involved.

e.g. for an elimination bimolecular, **E_2** reaction mechanism

$CH_3CH(Cl)CH_3 \xrightarrow[\text{reflux}]{KOH/EtOH} CH_3CH = CH_2$

$KOH + EtOH \longrightarrow EtO^-K^+ + H_2O$ then $EtO^-K^+ \longrightarrow EtO^- + K^+$

or $KOH \longrightarrow K^+ + OH^-$ then $EtOH + {}^-OH \longrightarrow EtO^- + H_2O$



$K^+ + Cl^- \longrightarrow KCl$

In this reaction, both removal of a halogen and formation of a double bond take place at the same time. This is because there is no hindrance to the processes taking place.
The above mechanism is **elimination bimolecular (E_2)** because two particles or species (i.e. EtO^- and the halogeno alkane) are involved in the rate determining step.
Note:
- For secondary halogeno alkanes, either the E_1 or the E_2 mechanisms may be used.
- Tertiary halogeno alkanes undergo E_1 mechanism due to steric hindrance.
- Rate of reaction depends on the strength of the carbon – halogen bond. It will be fastest with iodo halogeno alkanes and slowest with chloro halogeno alkanes.
This is because the *atomic radii of the halogens increases* from chlorine to iodine. This *increases covalent bond length* between the halogen and carbon atom, hence *bond strength decreases* in the order C–Cl > C–Br > C–I. This implies that the C-I bond will most easily be broken and the reaction will take place fastest with iodo halogeno alkanes.

c) **By partial reduction of alkynes**
(i) An alkyne (especially higher alkynes) can be reduced by hydrogen to form an alkene which is effectively isolated using a poisoned catalyst (Lindlar catalyst) e.g. $Pd/CaCO_3$ plus quinoline.

$$RC{\equiv}CH + H_2 \xrightarrow{\text{Lindlar catalyst}} RCH = CH_2$$

(ii) An alkyne and hydrogen in equimolar ratios are passed over a catalyst.
Catalysts that may be used are;
- Nickel at 150^{o}C - Platinum or Palladium at room temperature
i.e.

$$RC{\equiv}CH + H_2 \xrightarrow[150^oC]{Ni} RCH = CH_2$$

Note: Hydrogen gas should not be in excess.

d) **Dehalogenation of vicinal or germinal dihalides**
Vicinal dihalides are halogeno compounds with two halogen atoms on adjacent carbon atoms. Germinal dihalides are halogeno compounds with two halogen atoms on the same carbon atom.
(i) The dehalogenation of vicinal halides takes place when the dihalide is heated with zinc dust in an alcohol. e.g.

$$CH_3\,\underset{\displaystyle X}{\underset{|}{CH}}\,CH_2X + Zn \xrightarrow[heat]{CH_3\,OH\ (Alcohol)} CH_3\,CH = CH_2 + ZnX_2$$

(ii) The dehalogenation of germinal dihalides takes place when the dihalide is heated with zinc dust or metallic sodium in presence of an alcohol. It gives rise to higher alkenes (alkenes with a longer chain of carbon atoms). e.g.

$$CH_3\,\overset{\displaystyle x}{\overset{|}{\underset{\displaystyle x}{\underset{|}{C}}}}\,H \xrightarrow[alcohol,\ heat]{Zn\ dust\ (or\ Na)} CH_3\,CH = CH\,CH_3$$

Chemical Properties of Alkenes

The most characteristic reactions of unsaturated compounds are those in which the multiple bond is opened and new groups are attached to give saturated compounds.

Such reactions are classified as *additional reactions*. The localized pie bond electrons are more exposed than the sigma bond electrons and are therefore more vulnerable and available to be attacked by electron deficient species called *electrophiles*. Thus alkenes undergo mainly ***electrophilic addition reactions.***

(1) **Addition Reactions:**

Ionic addition reactions across the double bond are *initiated by a more electropositive* (electron deficient) part (atom) of the attacking reagent or molecule.

The more electropositive atom from attacking molecule then attaches itself to one of the unsaturated carbon atoms (those that contain the double bond) inducing a positive charge on the adjacent carbon atom. A carbocation is formed as an intermediate product together with a negatively charged particle (anion). The double bond is converted to a single bond.

The reaction mechanism is generally completed by subsequent attack of the anion onto the carbocation forming a neutral saturated product.

(a) Addition of **hydrogen (hydrogenation)**

The reaction takes place on the surface of a metal catalyst like Nickel, Platinum or Palladium. When Nickel is used, the reaction is carried out at 150^{o}C, while platinum and palladium being more active catalysts, the reaction is carried out at room temperature.

i.e. $>C=C< + H_2 \xrightarrow{\text{catalyst}} H-C-C-H$

e.g. $CH_3CH = CH_2 + H_2 \xrightarrow[150^{o}C]{Ni} CH_3CH_2CH_3$

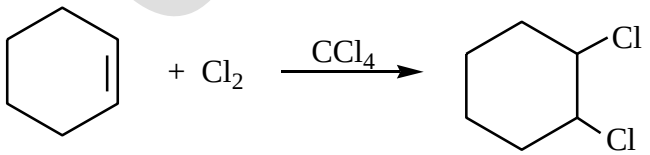
(b) Addition of **halogens (halogenation)**

Halogens such as Cl_2, Br_2 or I_2 are readily added to alkenes in presence of a non – polar solvent to give saturated products. The order of reactivity of the halogens for a given alkene is $Cl_2 > Br_2 > I_2$

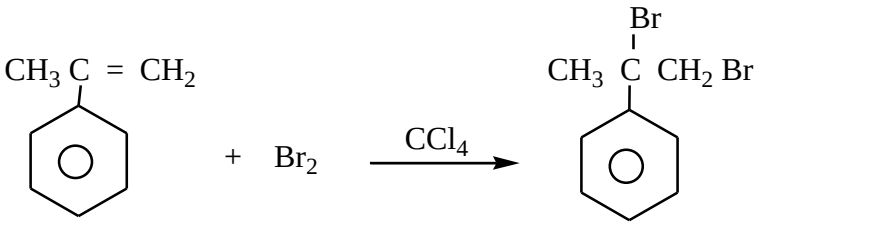
(i) In **presence of an inert solvent** e.g. CCl_4 or $CHCl_3$, a dihalogen product is formed.

e.g. $CH_3CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3\overset{Br}{\overset{|}{C}}HCH_2Br$

(1, 2 - dibromo propane)



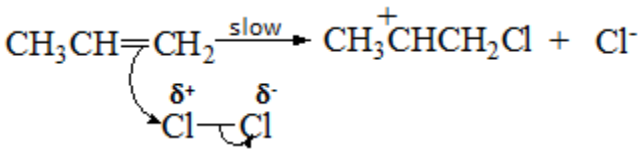
(1, 2 - dichloro cyclo hexane)

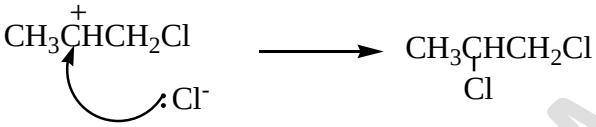


(2 - phenyl propene) (1, 2 - dibromo - 2 - phenyl propane)

Mechanism; (Is similar for all alkenes)

e.g. a)- for $CH_3CH = CH_2 + Cl_2 \xrightarrow{CCl_4} CH_3CHCH_2Cl$ (Cl)

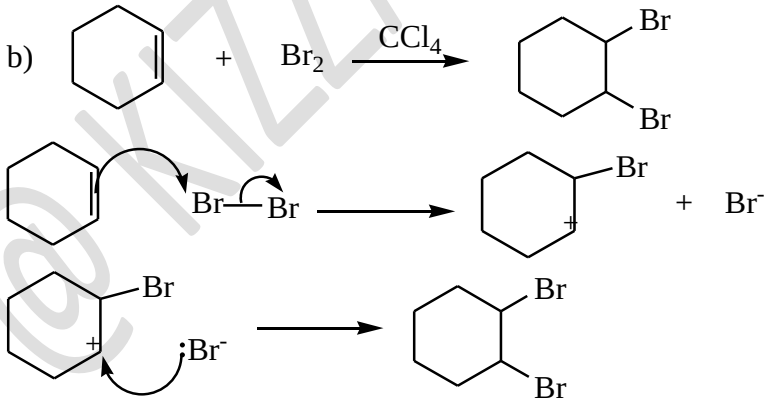




As the chlorine molecule approaches the double bond in the alkene, the pie bond electrons repel and distort the electron cloud of the chlorine molecule. This induces a partial positive charge on the chlorine atom closer to the double bond and a partial negative charge on the other chlorine atom. i.e. temporary dipoles are formed.

The chlorine atom (from the chlorine molecule) with the partial positive charge is electropositive (electron deficient) and hence attaches itself to the carbon atom of the double bond with more hydrogen atoms.

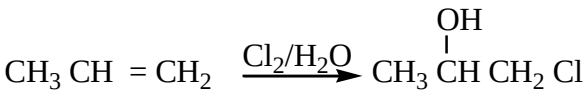
The double bond is then broken to form a secondary carbocation which is more stable. This occurs for all asymmetrical alkenes.



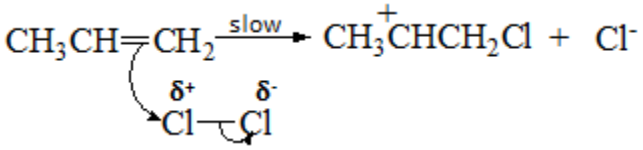
(ii) In **presence of water** as the solvent, a halogeno alcohol is produced as the main organic product.

This is because, after the formation of the carbo cation during the reaction mechanism, two types of nucleophiles are present i.e. the halide ion (X^-) and water (H_2O). One is a charged (negative) nucleophile and the other is a neutral nucleophile. Both are electron rich and compete for the electrophilic site on the carbocation (the positive charge on the carbo cation).

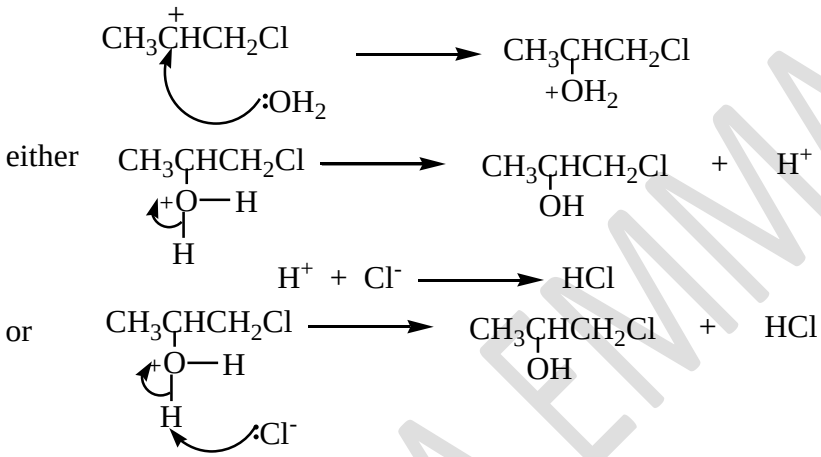
However, because water is the solvent which is polar, hence active, it is assumed to be in excess and has a higher concentration than the halide ion. Hence water competes more favourably for the electrophilic site, thus attaches to the positively charged carbon atom in preference to the halide ion. This is then followed by loss of a proton. e.g.



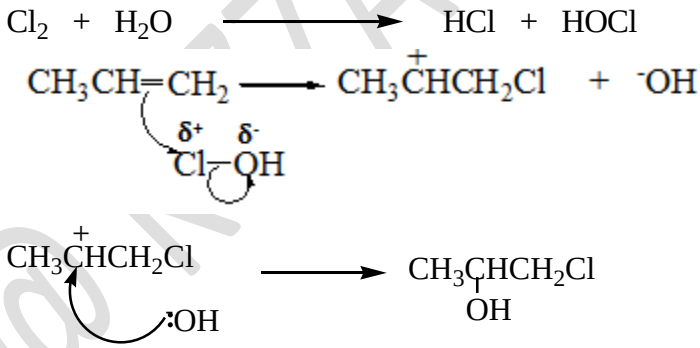
Mechanism



But since water is a solvent that is polar, the $[H_2O] > > [Cl^-]$, the H_2O is attacked by the carbocation.



The alternative mechanism



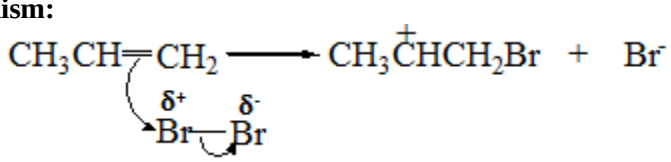
Note: The above reaction with alkenes specifically Br_2 in water (and sometimes CCl_4) is used to test for unsaturation (a double or triple bond).
In this reaction, the bromine which is brown is decolourised i.e. it turns from brown to colourless if an alkene or alkyne as a functional group is present.

(iii) When halogenation with **Br_2 is carried out in presence of NaCl solution**, a bromo chloro product is formed as the main product.
Similarly halogenation with **I_2 in presence of NaCl or NaBr solution,** a chloro – iodo product or bromo – iodo product is formed respectively.

This is because, during the course of reaction, two nucleophiles are formed which compete for the reaction electrophilic site. The strength of the Cl^-, Br^- and I^- are in order $Cl^- > Br^- > I^-$.
e.g.

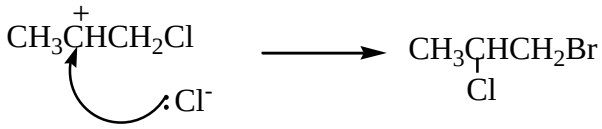
$$CH_3CH = CH_2 \xrightarrow{Br_2/NaCl} CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2Br$$

Mecahnism:



But $NaCl \longrightarrow Na^+ + Cl^-$

and the Cl^- ion is in solution as an ionic (polar) solvent, it's more reactive and hence a stronger nucleophile than the Br^- ion



$Na+ + Br^- \longrightarrow NaBr$

Note: In the 1st step of halogenation reactions, the two electrons which form the new bond are both provided by the double bond in the alkene. Thus the halogen in this case described as an *electron seeking (electrophilic)* particle.

(c) Addition of **halogen acids** (HCl, HBr or HI)

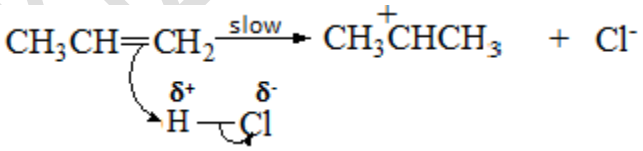
(i) In **absence** of an organic peroxide; Markwonikoff's rule can be used to predict the product. The reaction proceeds via an ionic mechanism.

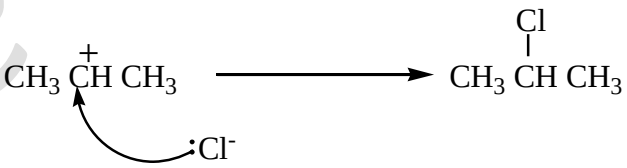
i.e.

$$RCH = CH_2 + HX \longrightarrow R\underset{\displaystyle X}{\underset{|}{C}}HCH_2$$

e.g.

$$CH_3CH = CH_2 + HCl \longrightarrow CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3$$





Note: In addition reaction of unsymmetrical reagent across an asymmetrical (unsymmetrical) alkene, (i.e. alkenes whose carbon atoms that carry the double bond have different numbers of hydrogen atoms), the hydrogen atom or the more electropositive atom from the reagent becomes attached to the carbon atom of the double bond possessing the greater number of hydrogen atoms while the more electronegative becomes attached to the carbon atom with less number of hydrogen atoms or without hydrogen atoms.

This is known as Markovnikov's rule put forward by the Russian chemist Vladimir Markovnikov in 1870.

The rule is based on formation of more stable carbocations during the course of the reaction. Tertiary carbocations are most stable, followed by secondary carbocations while primary carbocations are the least stable.

It can also be used for other addition reactions to predict the products.

(ii) In **presence of an organic peroxide** (and uv light or high temperature) the product is predicted using anti Markwonikoff's rule for **addition of HBr only** and the reaction proceeds via a free radical chain mechanism. i.e.

$$RCH = CH_2 + HBr \xrightarrow[uv]{\text{Organic peroxide}} RCH_2CH_2Br$$

Hydrogen chloride and hydrogen iodide do not react against Markovnikov's rule. This is because, halogen free radicals (free radical chain reaction), hydrogen ions and halide ions (for ionic reaction) are formed. However, although halogen free radicals are generated in the initiation stage, the steps under the propagation stage are so slow such that the overall rate of the chain reaction is slower than that of electrophilic addition ionic reaction.

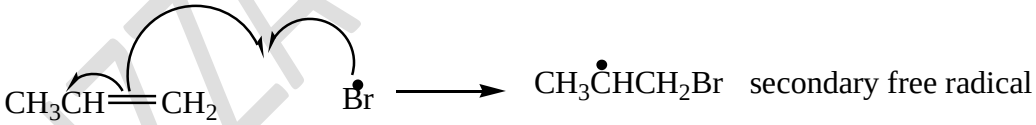
The common organic peroxide used is di(benzene carbonyl) peroxide also referred to as di(benzoyl) peroxide. The organic peroxide is represented as ROOR where R is an alkyl group, acyl group or phenyl group. e.g.

$$CH_3CH = CH_2 + HBr \xrightarrow{ROOR} CH_3CH_2CH_2Br$$

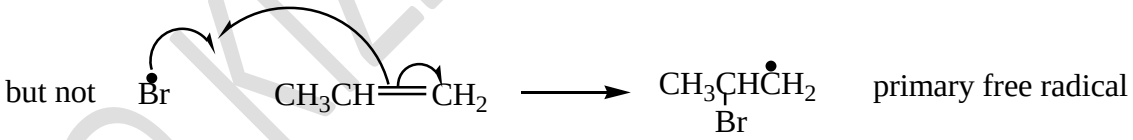
Mechanism

Initiation

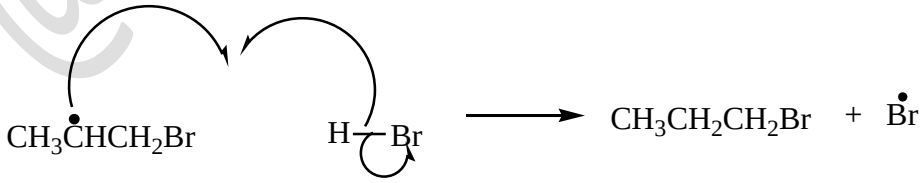
Propagation



but not



The reaction will proceed more steadily with the secondary free radical giving a high yield. This because, the secondary free radical is more stable than the primary free radical.



Termination

Note: *(a)* Addition of HCl or HI in presence of a peroxide does not follow anti Makwonikoff's rule. The product is therefore predicted by use of the Markwonikoff's rule and ionic mechanism id followed.

(b) The halogen acid can be generated in situ by action of concentrated sulphuric acid on sodium halides.

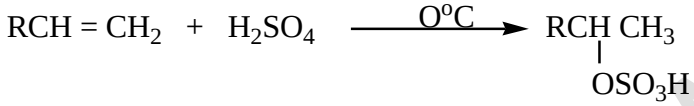
(c) Anti Markovnikov's products may also be obtained:

- in presence of strong electron withdrawing substituents such as fluorine in the alkene (e.g fluoroethene).

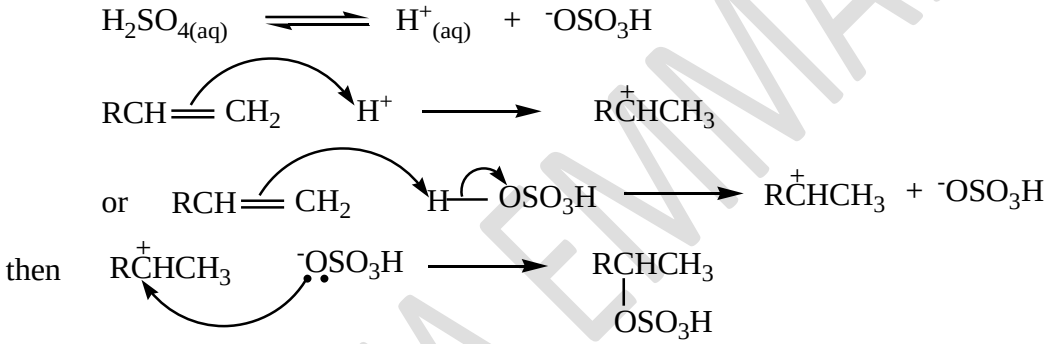
- when steric hindrance takes place. This prevents completion of the reaction by attachment of larger, more electronegative species at a highly substituted carbon atom.

(d) **Addition of hydrogensulphate or water** to alkenes.

(i) Addition of concentrated sulphuric acid in cold (0 - 15°C) to form alkyl hydrogen sulphates.

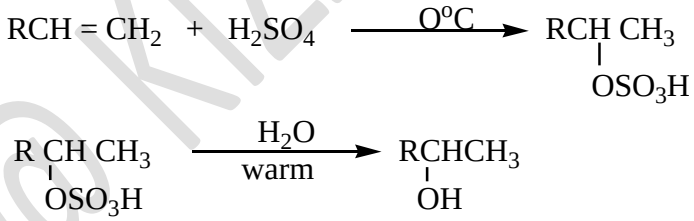


Mechanism

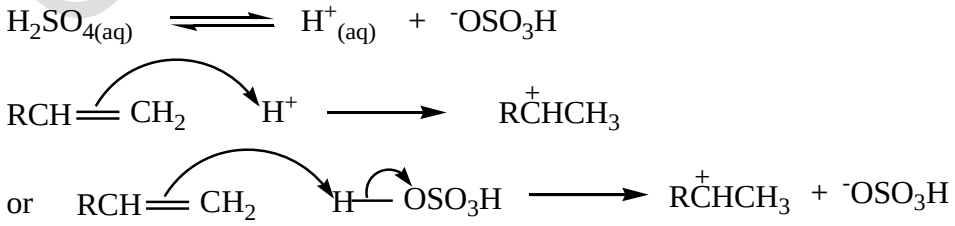


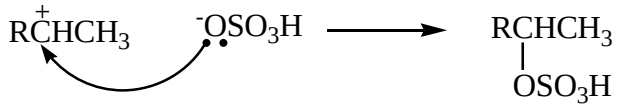
(ii) Addition of concentrated sulphuric acid followed by heating in water (hydrolysis).

Alkenes react with concentrated sulphuric acid in cold (0 - 15°C) to form alkyl hydrogen sulphates, and on diluting the product (addition of water) followed by warming, an alcohol is produced. i.e.

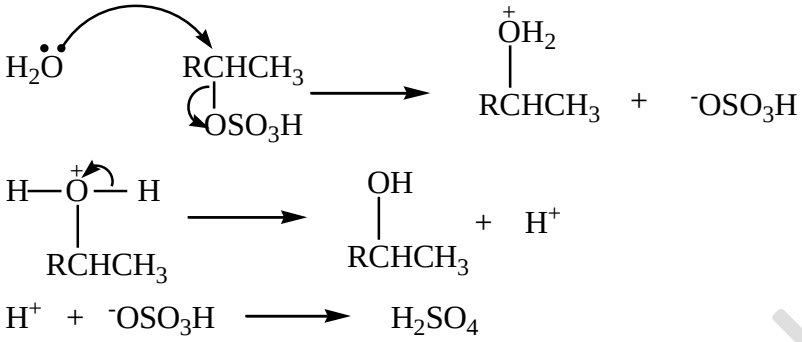


Mechanism



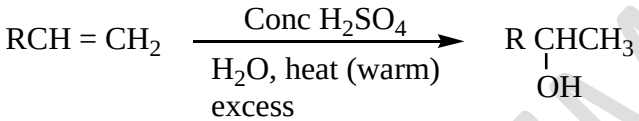
then 

But on diluting with water and warming, $[H_2O] > > [^-OSO_3H]$ hence H_2O replaces $^-OSO_3H$.

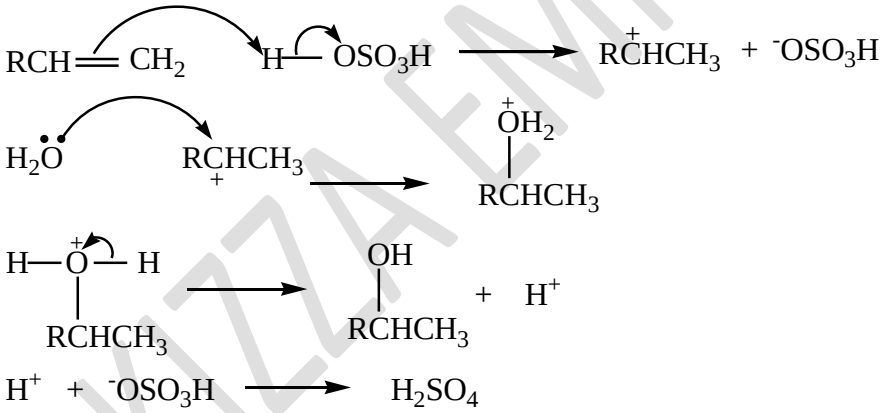


Note:

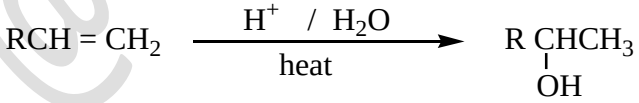
- If the reagent and conditions are mixed and warmed concurrently with the alkene, one equation may be written as shown below;



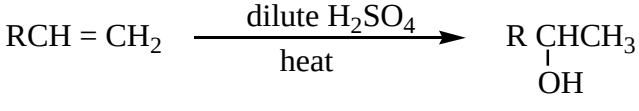
Mechanism:



- Concentrated sulphuric acid provides H^+ which starts the reaction but it is regenerated at the end hence remains chemically unchanged. It thus acts as a catalyst. H_2SO_4 is sometimes represented merely as H^+.

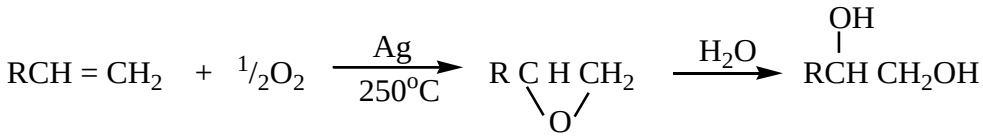


The same reaction and mechanism occurs when the alkene is warmed / heated in dilute sulphuric acid.



(e) **Reaction with Oxygen**

Alkenes react with oxygen over heated silver catalyst to form an epoxide which later on hydrolysis forms a diol.



In absence of the catalyst, CO_2 or CO or C and water are formed.

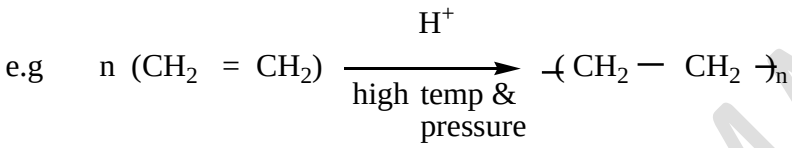
(f) **Polymerisation of alkenes**

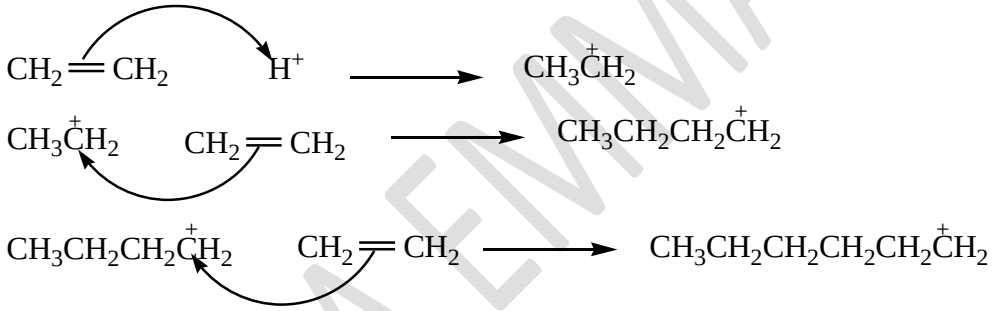
Simple alkenes can be polymerized to form macro molecular compounds with the same empirical formula as the monomer. They undergo ***addition polymerization.***

Conditions for polymerization of alkenes include;

- High temperature $\cong 120^oC$
- High pressure
- Presence of catalyst e.g. oxygen catalyst, peroxide, acid catalyst or Ziegler catalyst [mixture of $(CH_3CH_2)_3Al$ and $TiCl_4$]

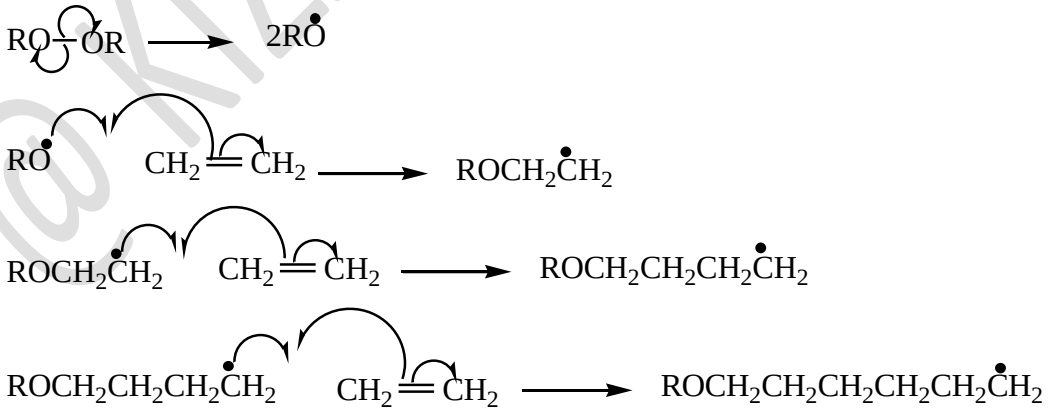
(i) **Ionic mechanism**





etc, until n moles have polymerized.

(ii) **Free radical chain mechanism**



etc until n moles have been combined.

(2) <u>Oxidation reactions</u>

A. Alkenes undergo oxidation by potassium manganate(VII) solution.

(a) ***In Alkaline conditions***

The *purple colour of potassium manganate(VII) changes to brown* due to formation of manganese(IV) oxide and the alkene forms a diol (glycol). i.e.

$$RCH = CH_2 \xrightarrow{MnO^-_4/OH^-} RCH(OH)CH_2OH$$

(b) ***In acidic conditions***

The *purple colour of potassium manganate(VII) changes to colourless.*

(i) When the alkene is in excess and the oxidizing agent is in limited supply, a diol (glycol) is formed. This is known as hydroxylation. i.e.

$$\underset{\text{excess}}{RCH = CH_2} \xrightarrow{MnO^-_4/H^+} RCH(OH)CH_2OH$$

(ii) When heated and the oxidizing agent is in excess, oxidative cleavage occurs, yielding carbonyl compounds (i.e. aldehydes and ketones).

The aldehydes formed in this way are further oxidized to carboxylic acids.

N.B: Methanoic acid from methanol is further oxidized to carbondioxide and water.

i.e. $RCH = CH_2 \xrightarrow[\text{heat}]{\text{excess } MnO_4^- / H^+} RCHO + HCHO$

$RCHO \xrightarrow{\text{further oxidised}} RCOOH$; $HCHO \xrightarrow{\text{further oxidised}} HCOOH \longrightarrow CO_2 + H_2O$

i.e. $RCH = CH_2 \xrightarrow[\text{heat}]{\text{excess } MnO_4^- / H^+} RCOOH + CO_2 + H_2O$

e.g. $CH_3C(CH_3) = CHCH_3 \xrightarrow[\text{heat}]{\text{excess } MnO^-_4 / H^+} CH_3COCH_3 + CH_3CHO$

(ketone) propanone; (aldehyde) ethanal — oxidised further

then CH_3CHO (ethanal) $\xrightarrow{\text{further oxidation}} CH_3COOH$ (ethanoic acid)

Over all equation thus is;

$$CH_3C(CH_3) = CH\,CH_3 \xrightarrow[\text{heat}]{\text{excess } MnO_4^- / H^+} CH_3COCH_3 + CH_3COOH$$

It is observed from these reactions that the excess oxidizing agent cleaves or breaks the double bond and establishes itself as the new link to each fragment.

As a result, the oxidation reactions cannot only be used to establish presence of a double bond but also used establish/locate the position of the double bond in the alkene by identification (analysis) of the products.

e.g. CH_3CHO and $HCHO$ are from $CH_3\,CH = CH_2$

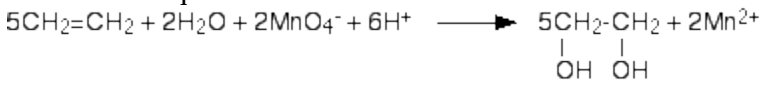
CH_3COCH_3 and CH_3CHO are from $CH_3C(CH_3) = CHCH_3$

Note:

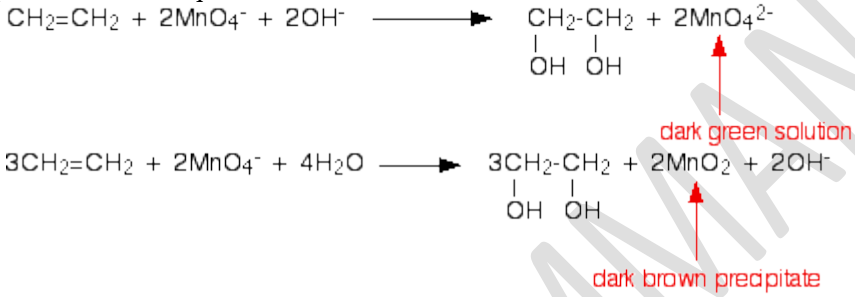
i) Oxidation reactions can be used to identify
- presence of a double bond (an alkene)
- the location of a double bond in an alkene molecule.

ii) Hydroxylation (formation of a diol) of alkenes may also be brought about by:
- Using osmium tetraoxide in presence of ether followed by addition of aqueous Na_2SO_3.
- Warming the alkene with hydrogen peroxide and ethanoic acid.

iii) Under acidic conditions, the manganate(VII) ions are reduced to manganese(II) ions. An example of the full equation is shown below:



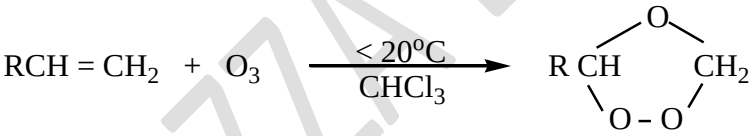
iv) Under alkaline conditions, the manganate(VII) ions are first reduced to green manganate(VI) ions and then further to dark brown solid manganese(IV) oxide (manganese dioxide). An example of the full equations is shown below:



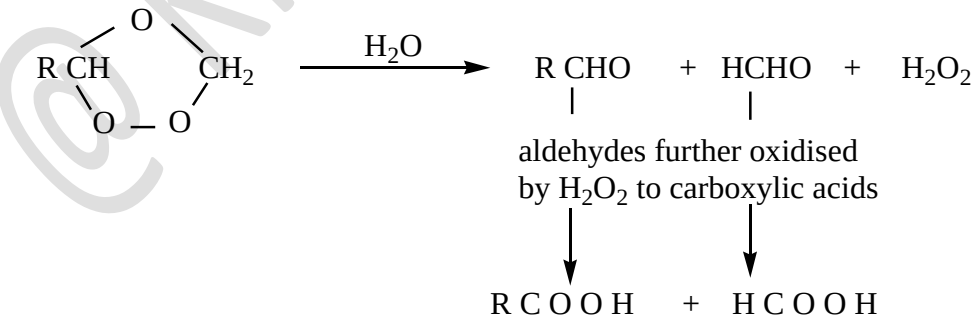
B. **Ozonolysis of alkenes**

Reaction with ozone (tri oxygen or ozonised oxygen) followed by hydrolysis.

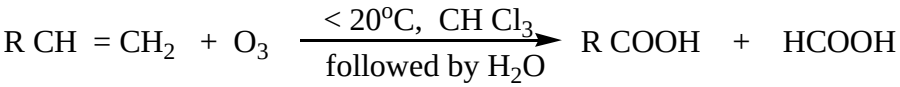
Ozone adds across the double bond to form an ozonide. The ozonide is unstable and explosive hence prepared below 20°C in a non – polar solvent like chloroform (trichloromethane), $CHCl_3$ or carbon tetrachloride (tetrachloromethane), CCl_4.



The unstable ozonide is then readily hydrolysed by water, splitting into two carbonyl compounds and H_2O_2. If the carbonyl compound is an aldehyde, it is oxidized by H_2O_2 to form a carboxylic acid. i.e.



Hence overall reaction is;



Note:

i) If a ketone is formed it cannot be further oxidised.

e.g $CH_3CH_2\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CHCH_3 + O_3 \xrightarrow[\text{followed by } H_2O]{< 20^oC,\ CCl_4} CH_3CH_2\overset{\displaystyle O}{\overset{\displaystyle ||}{C}}CH_3 + CH_3COOH$

ii) When Zinc and ethanoic acid are used during hydrolysis, the possibility of further oxidation is avoided, as the product stop at the carbonyl stage.

i.e. $RCH = CH_2 + O_3 \xrightarrow[\text{then } Zn/H_2O]{< 20^oC,\ CHCl_3} R\,CHO + HCHO + H_2O_2$

The presence of Zinc prevents H_2O_2 from oxidizing any aldehyde that may be formed.