

Physical Properties of Alkenes

Kumud Bala

Physical state, colour, smell: The first three members of the family i.e., ethene, propene and butene are colourless gases; the next fourteen members (C_5-C_{18}) are liquids while the higher ones are solids. Except ethene which has a pleasant smell, all other alkenes are colourless and odourless gases.

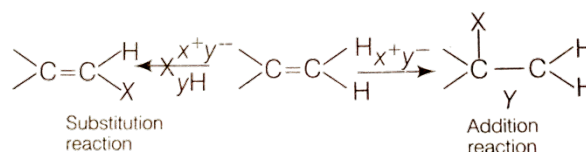
Solubility: They are insoluble in water, but are fairly soluble in non polar solvent such as benzene petroleum ether, etc.

Boiling point: Their boiling points increase regularly with increase in molecular mass. On the average, the boiling points generally increase by 20-30 K for the addition of each $-CH_2$ group to the chain. Like alkanes, straight chain alkenes have higher boiling points than isomeric branched chain alkenes.

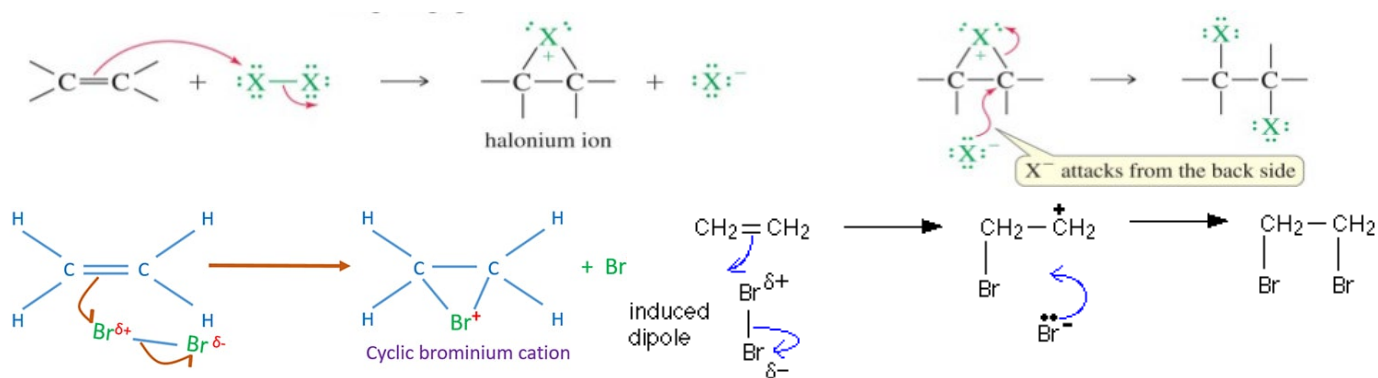
Why do alkenes undergo electrophilic addition reaction?

Alkenes are characterized by the presence of double bond which consists of a strong carbon-carbon σ -bond and a weak carbon-carbon π -bond. The π -electrons form an electron cloud which lies above and below the plane of σ -bonded carbon atoms. These, π -electrons are, therefore, more exposed and hence are less tightly held between the two carbon atoms. Since the electrons are negatively charged particles, therefore, the π -electrons attract the electrophiles and repel nucleophiles. In other words, alkenes undergo electrophilic reactions. Electrophilic reactions can be of two types' (i) addition and (ii) substitution

In electrophilic substitution reactions one σ -carbon-hydrogen bond is broken and a new σ -bond between one of the doubly bonded carbon atoms and the electrophile is formed. Since the bond energies of σ -C-H broken bond and newly formed σ -C-X bond are not much different, therefore electrophilic substitution reactions are not accompanied by large energy changes. In electrophilic addition reactions, one weak π -bond (251 kilojoules per mole) is broken and two strong σ -bonds ($2 \times 348 = 696$ joules per mole) are formed. The overall reaction is accompanied by a release of about (696 - 251) 445 kilojoule per mole of energy. In other words, electrophilic addition reactions are energetically more favorable than electrophilic substitution reactions. Thus, the typical reactions of alkenes are electrophilic addition reactions and not the electrophilic substitution reactions.

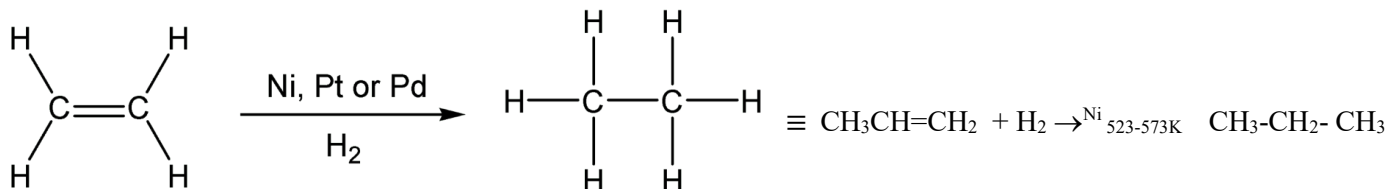


Mechanism:



Chemical reactions of alkene:

Addition reactions of alkenes: addition of dihydrogen to unsaturated hydrocarbon (such as alkene and alkyne) is called catalytic hydrogenation. Alkene readily add dihydrogen in the presence of raney nickel, platinum, palladium as catalyst at room temperature or ordinary medical at 523- 573 K to form alkanes (Sabatier and Senderen's reduction). For example,

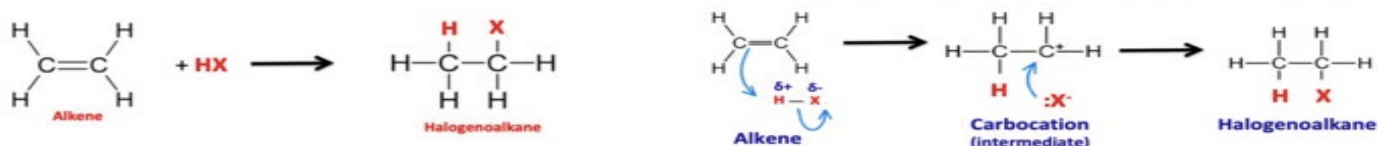


Addition of halogens: Halogens such as chlorine and bromine readily add to alkenes to form 1,2-dihaloalkanes. For example,

During the addition of bromine to alkenes, the orange red colour of bromine is discharged since the di bromide formed is colourless. This reaction is therefore, used as a test for unsaturation in organic compounds. Fluorine reacts with alkenes too readily to be controlled in the laboratory while iodine does not react with alkene at ordinary temperatures. Thus, the order of reactivity of addition of halogen to alkene is fluorine > chlorine > bromine > Iodine.

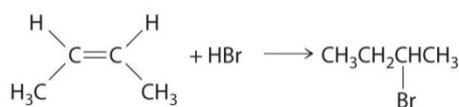


Addition of hydrogen halides: Alkene reacts with hydrogen halides (HCl, HBr, HI) to form monohaloalkanes called alkyl halides.

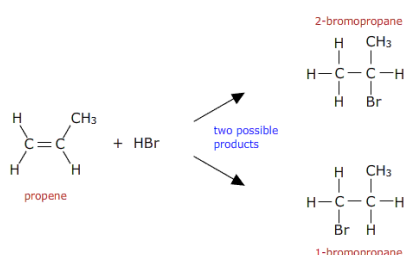
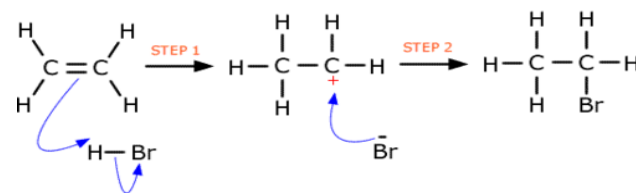


The order of reactivity of hydrogen halides in the reaction is: HI > HBr > HCl. This order of reactivity can be explained on the basis of bond dissociation energy of the hydrogen halides: HI (300 kJmol⁻¹) > HBr 360 kJmol⁻¹) > HCl (430 kJmol⁻¹). The actual product formed, however, depends upon whether the alkene is symmetrical or unsymmetrical as discussed below:

Addition to symmetrical alkenes: When the alkene is symmetrical only one product is theoretically possible. For example,



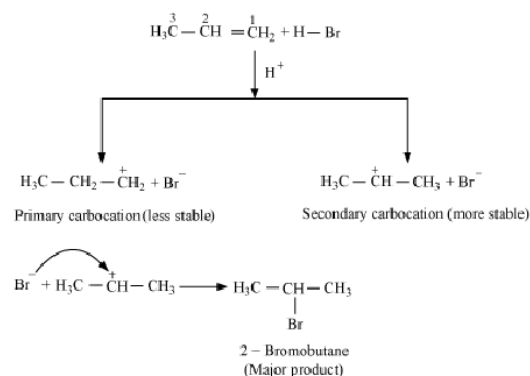
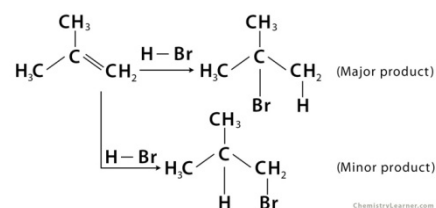
Mechanism: Like the addition of halogens, addition of hydrogen halides to alkene is also an electrophilic addition reaction and occurs by the following two steps:



Addition to unsymmetrical alkenes:

When the alkene is unsymmetrical, two products are theoretically possible. For example, the addition of HBr to propene in the dark and in the absence of peroxide can give two products. But experimentally, it has been found that under these conditions, the major product is 2 -bromopropane and the minor product is 1 -bromopropane.

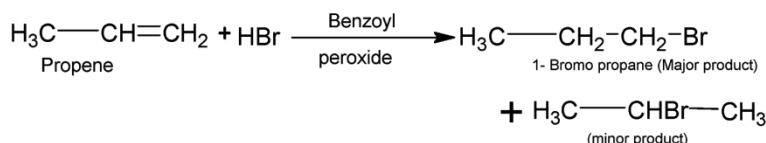
Markovnikov's rule: Markovnikov, a Russian chemist, studied a large number of such addition reactions and postulated an empirical rule in 1869 which is known after his name as Markovnikov's rule. The rule states that 'The addition of unsymmetrical reagents such as HX, H₂O, HOX, etc. to unsymmetrical alkenes occurs in such a way that the negative part of the addendum (i.e., adding molecule) goes to that carbon atom of the double bond which carries lesser number of hydrogen atoms.'



Theoretical explanation of Markovnikov's rule: The addition of halogen halides to alkene is an electrophilic addition reaction. Thus, during the addition of HBr to propene, the first step involves the addition of a proton. This addition, in principle, can occur in two ways. If the proton adds on the terminal carbon atom of the double bond, secondary carbocation (I) is formed and if the addition occurs on the middle carbon atom, a primary carbocation (II) is produced.

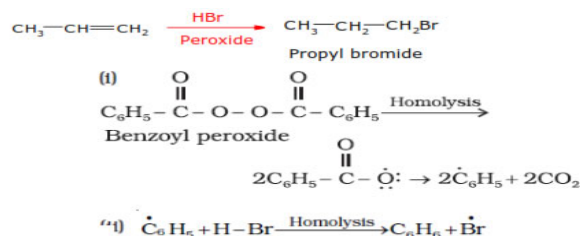
Since a 2° carbocation (I) is more stable than 1° carbocation (II), therefore, carbocation (I) is predominantly formed. This carbocation then rapidly undergoes nucleophilic attack by the Br⁻ ion forming 2-bromopropane as the major product. Thus, Markovnikov's addition occurs through more stable carbocation intermediate.

Peroxide effect: It may be noted that Markovnikov's rule is not always followed. The addition of HBr (but not of HCl or HI) to unsymmetrical alkene takes place in the presence of peroxides such as benzoyl peroxide (C₆H₅CO-O-O-COC₆H₅), contrary to Markovnikov's rule. This is known as Peroxide effect or Kharasch effect.

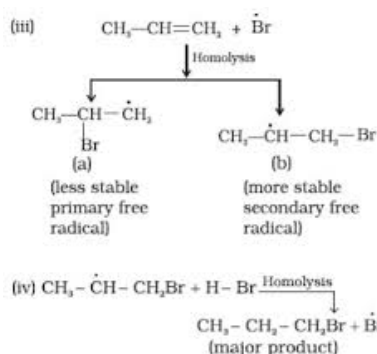


Mechanism: The addition of HBr to alkene in presence of peroxides occurs by a free radical mechanism. It consists of the following three steps:

(a) Initiation:

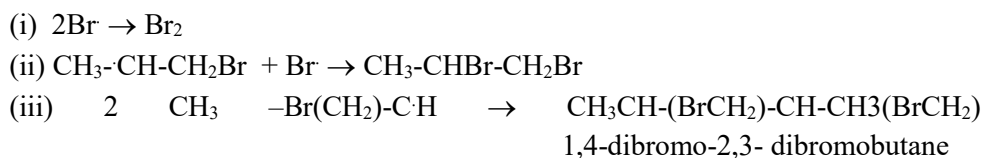


(b) Propagation: it consists of two steps. During the first step, a



Br adds to the double bond in such a way to give the more stable free radical. In the second step, the free radical thus produced abstracts a H from HBr to complete the addition.

(c) Termination:

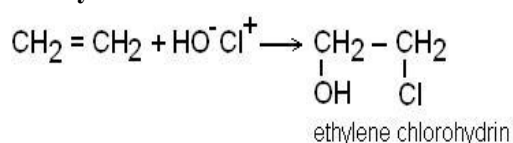


Exceptional behavior of HBr: To understand why peroxide effect is observed with HBr and not with HF, HCl or HI. Let us consider the ΔH of the two propagation steps.

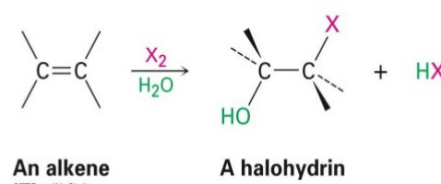
X in HX	ΔH (in kJ/mol)	ΔH (in kJ/mol)
	(i) $X + CH_2=CHCH_3 \rightarrow XCH_2-CH-CH_3$	(ii) $XCH_2-CHCH_3 + HX \rightarrow XCH_2-CH_2CH_3 + X$
F	-209	+159
Cl	-101	+27
Br	-42	-37
I	+12	-104

From the above data, it is clear that only with HBr, both the steps are exothermic and hence the peroxide effect is observed. With HCl or HF, the peroxide effect is not observed because the second step involving the reaction of carbon radical with HCl or HF is endothermic. Further, the peroxide effect is also not observed with HI because the first step involving the addition of iodine radical to alkene is endothermic.

Addition of the elements of hypohalous acids (HOX where X = Cl, Br or I)-halohydrin formation: Chlorine and bromine in the presence of water readily

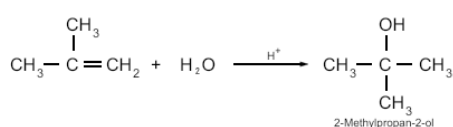


add to alkene to form the corresponding halohydrins.

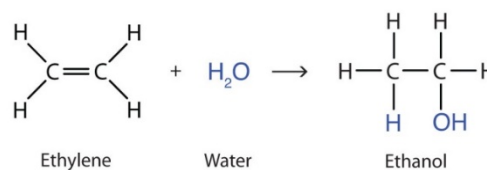


The overall reaction involves the addition of the elements of hypohalous acid (HO-X) in accordance with Markovnikov's rule. The order of reactivity of different haloacids, i.e., Cl_2/H_2O (HOCl) > Br_2/H_2O (HOBr) > I_2/H_2O (HOI)

Addition of water: (direct hydration of alkene) : Hydration means addition of water. Ordinarily, water does not add directly to most of alkenes. However, some reactive alkenes do

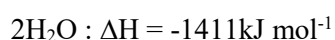


add water in presence of mineral acids to form alcohols. The addition occurs in accordance with Markovnikov's rule. For example,



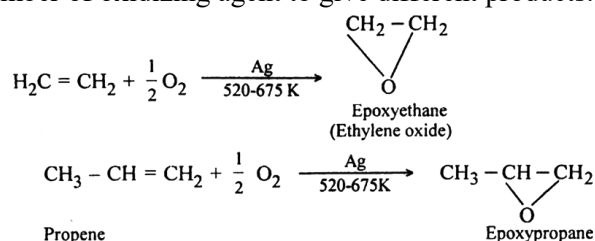
Oxidation reactions of alkene:

- (i) Complete oxidation with oxygen or air-combustion- Alkenes burn in oxygen or air to form carbon dioxide. This process is called combustion. All combustion reactions are highly exothermic in nature. For example-

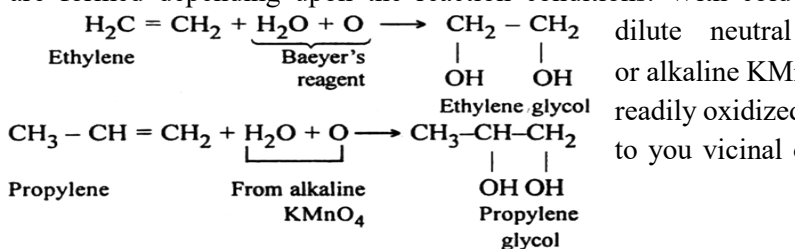


- (ii) Control oxidation with oxidizing agent: Alkenes react with a number of oxidizing agent to give different products:

(a) **Oxidation with oxygen:** alkenes react with oxygen in the presence of silver as a catalyst to form epoxyalkanes or epoxides. For example,

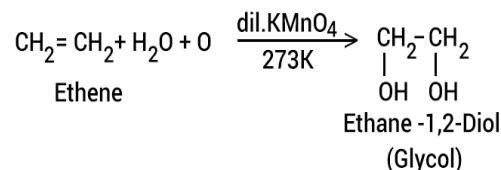


(b) **Oxidation with potassium permanganate:** Different products are formed depending upon the reaction conditions. With cold



dilute neutral or alkaline $KMnO_4$ -Because of the presence of π bonds, alkene are readily oxidized by cold dilute, neutral or alkaline $KMnO_4$ solution to you vicinal or 1,2-diols or 1,2 -glycols while $KMnO_4$ is itself

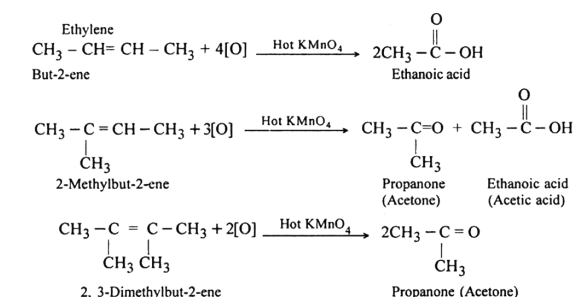
reduced to MnO₂. This reaction is called hydroxylation since during this process, two hydroxyl groups are added across the double bond. For example,



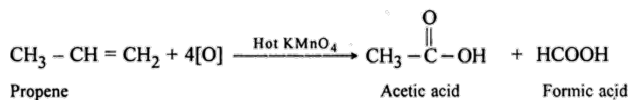
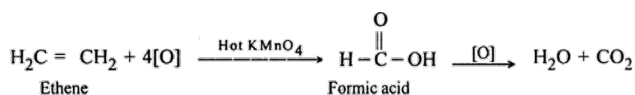
During this reaction the pink colour of the KMnO₄ solution is discharged and a brown precipitate of manganese dioxide is obtained. The reaction is, therefore, used as a test for unsaturation under the name Baeyer's test.

(c) Oxidation with hot KMnO₄ solution: When an alkene is heated with hot KMnO₄ solution, cleavage of the carbon = carbon double bond occurs leading to the formation of carboxylic acids, ketones and carbon dioxide depending upon the nature of the alkene as shown below:

With terminal alkenes, one of the product is always



Note. =C-R gets oxidised to RCOOH (acid). =C-R' gets oxidised to R'-C(=O) (ketone)

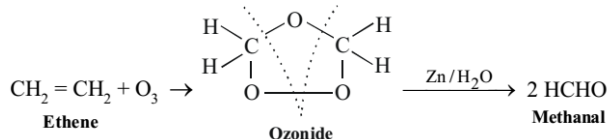


HCOOH $\xrightarrow{[\text{O}]}$ H₂O + CO₂
methanoic acid (formic acid) which on further oxidation gives carbon dioxide and water. For example,

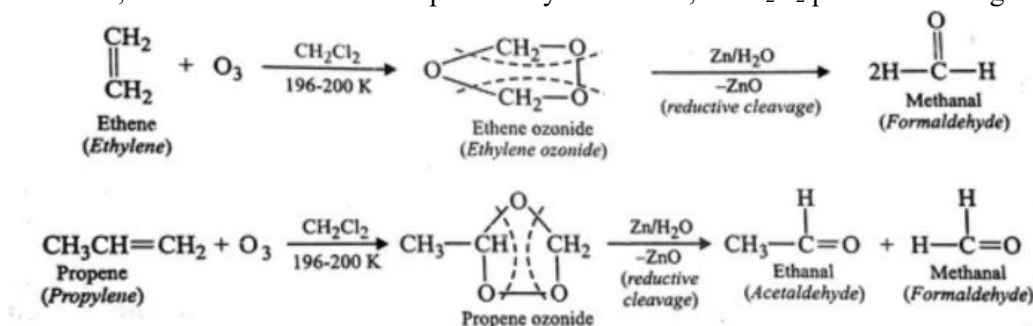
With non-terminal alkenes, carboxylic acids and ketones or both of these are obtained depending upon the nature of the alkene. For example,

(d) Oxidation with ozone: When ozone is passed through a

solution of an alkene in some inert solvent such as CH₂Cl₂, CHCl₃ or CCl₄ at a low temperature (196 – 200K), it oxidizes alkenes to ozonides. Ozonides are unstable and explosive. Therefore, they are not usually isolated but are reduced, in situ, with zinc dust and water or H₂/Pd to give aldehydes or ketones or a mixture of these (reductive cleavage) depending upon the structure of the alkene.



However, if the ozonides are decomposed only with water, the H₂O₂ produced during the reaction oxidized the initially



formed aldehydes to the corresponding acids (oxidative cleavage). These two -steps conversion of an alkene into an ozonide followed by its reductive cleavage to yield carbonyl compounds is called ozonolysis.

Importance: Ozonolysis is a versatile method for locating the position of a double bond in an unknown alkene since no two different alkenes give the same combination of aldehydes and ketones. Therefore, this method has been extensively used in the past for structure elucidation of alkenes. For example,

