Electrophilic addition reaction and their mechanism

Learning outcome

After studying this lecture, you shall be able to:

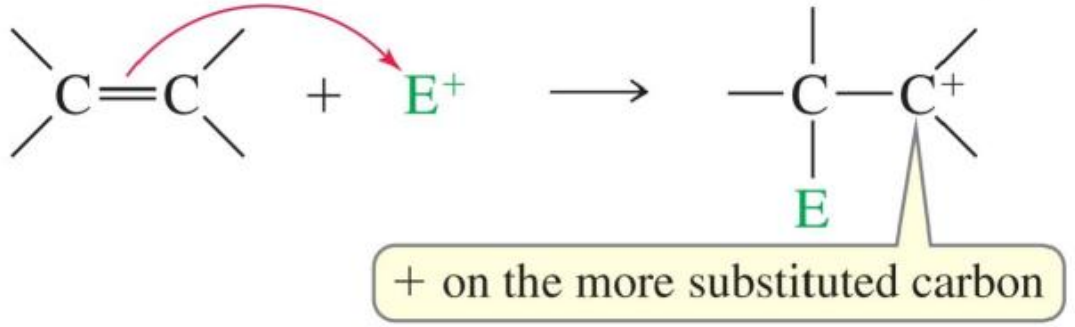
- Explain the electrophilic addition reaction
- Differentiate between markovnikov and anti markovnikov rule
- Explain the mechanism of markovnikov and anti markovnikov rule

Electrophilic addition reaction

- Addition reactions are those in which the attacking reagents adds upto the substrate molecule without elimination or substitution.
- These reactions are characteristics of compounds containing multiple bonds (double or triple bonds)
- An electrophilic addition reaction is a reaction in which a substrate is initially attacked by an electrophile, and the overall result is the addition of one or more relatively simple molecules across a multiple bond.

Electrophilic Addition

- Step 1: Pi electrons attack the electrophile.



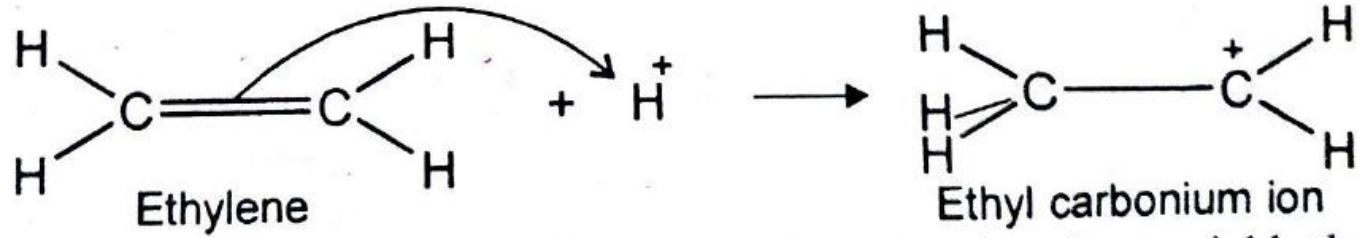
- Step 2: Nucleophile attacks the carbocation.

MECHANISM. The mechanism of the above reaction involves the following steps :

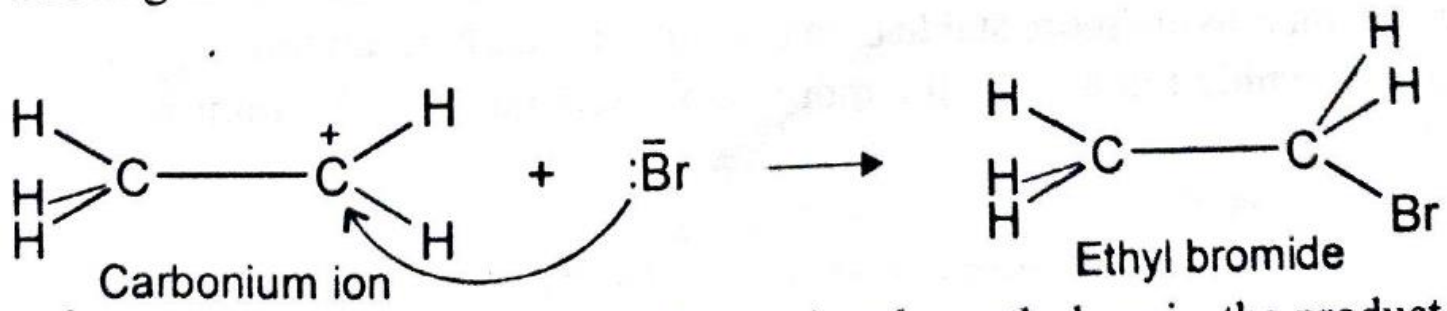
Step 1. HBr ionises to give a proton (electrophile) and a bromide ion (nucleophile).

$$HBr \longrightarrow \underset{\text{Proton}}{H^+} + \underset{\text{Bromide ion}}{:\bar{B}r}$$

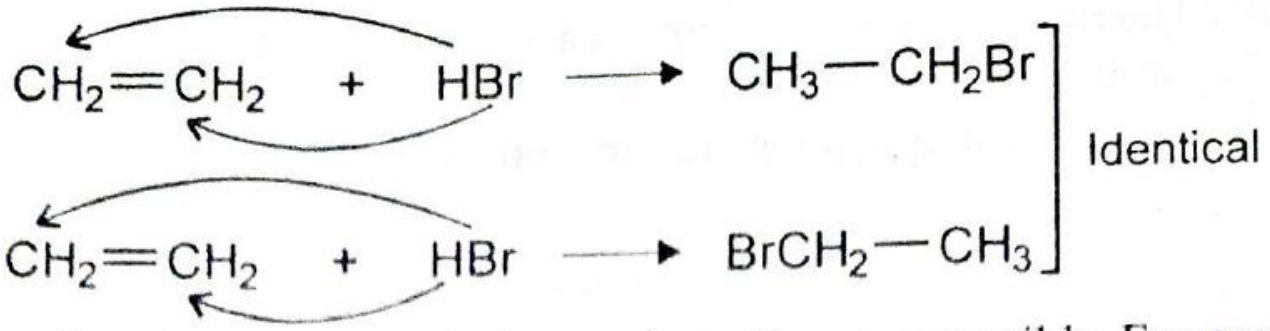
Step 2. The proton attacks the double bond to form ethyl carbonium ion.



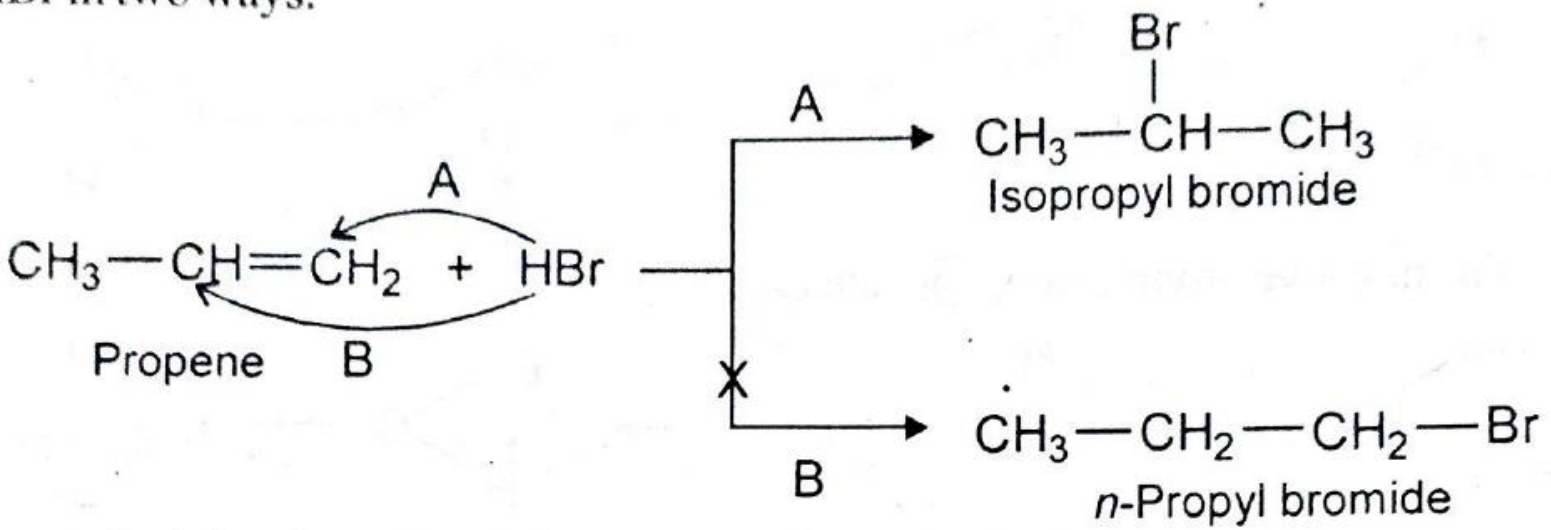
Step 3. The negative bromide ion, $:\bar{B}r$, attacks the carbonium ion to yield ethyl bromide.



When an alkene is symmetrical about the double bond, as ethylene is, the product formed is the same no matter which way H—Br becomes attached to the alkene.



If, however, the alkene is unsymmetrical, two alternatives are possible. For example, propene can react with HBr in two ways.



Experimentally it has been found that isopropyl bromide is the major product.

Markovnikov Rule. After studying a large number of such addition reactions, the Russian chemist Vladimir Markovnikov put forward the following rule :

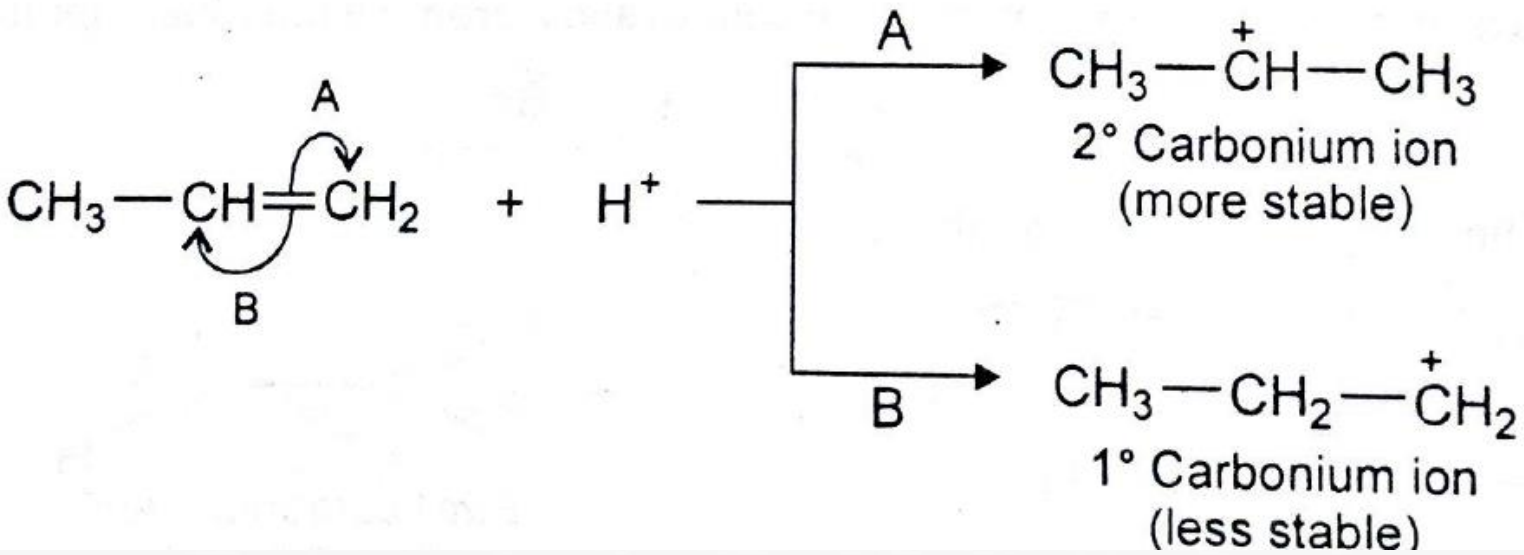
When an unsymmetrical reagent adds to an unsymmetrical alkene, the positive part of the reagent becomes attached to the double bonded carbon which bears the greatest number of hydrogen atoms.

MECHANISM. Markovnikov rule can be explained in terms of modern mechanistic theory. Consider the addition of HBr to propene. The mechanism of this reaction involves the following steps:

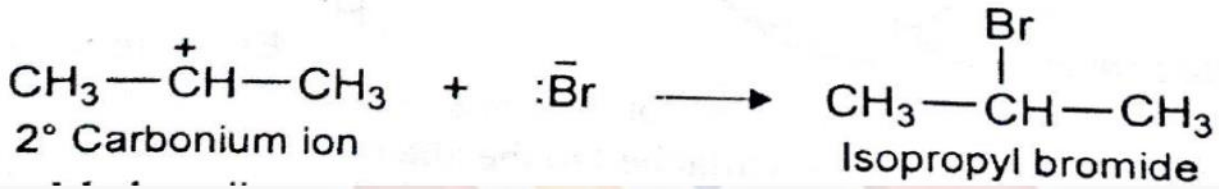
Step 1. HBr ionises to give a proton (electrophile) and a bromide ion (nucleophile).

$$HBr \longrightarrow \underset{\text{Proton}}{H^+} + \underset{\text{Bromide ion}}{:\bar{B}r}$$

Step 2. The proton attacks the double bond to form a more stable carbonium ion.

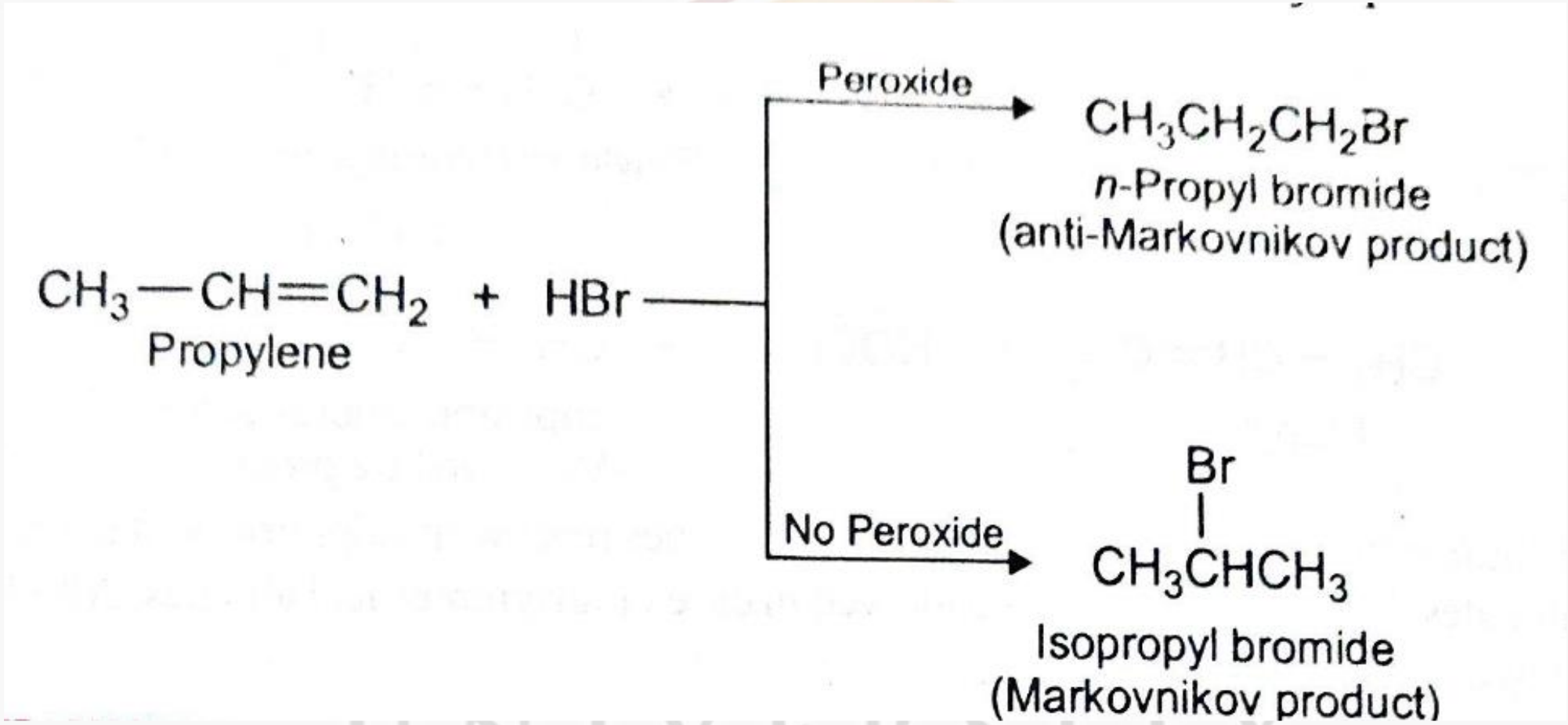


Step 3. The bromide ion attacks the more stable secondary carbonium ion to give the major product.



Anti Markonikov Rule or Peroxide effect:

- In 1933 the American M.S. Kharasch discovered that the addition of HBr to unsymmetrical alkenes in the presence of organic peroxides takes place in opposite position. This is also known as peroxide effect. For example when propylene reacts with HBr in the presence of a peroxide, the major product is n- propyl bromide where as in absence of peroxide the major product is iso propyl bromide.


Peroxide
CH3CH2CH2Br
n-Propyl bromide
(anti-Markovnikov product)
CH3—CH=CH2 + HBr
Propylene
No Peroxide
Br
CH3CHCH3
Isopropyl bromide
(Markovnikov product)

MECHANISM. Propylene reacts with HBr in the presence of a peroxide by a free radical mechanism. Following steps are involved :

Step 1. Peroxide dissociates to give alkoxy free radicals.

$$R{-}O{-}O{-}R \xrightarrow{\Delta} 2R{-}O\cdot$$

Step 2. Alkoxy free radical attacks HBr to form a bromine atom (a free radical).

$$R{-}O\cdot + H : Br \longrightarrow R{-}OH + Br\cdot$$

Step 3. Bromine atom can attack propylene to give a primary free radical and a secondary free radical.

$$Br\cdot + CH_3{-}CH{=}CH_2 \xrightarrow{(a)} CH_3{-}\underset{Br}{\underset{|}{CH}}{-}\dot{C}H_2$$

Propylene — 1° Free radical (less stable)

$$Br\cdot + CH_3{-}CH{=}CH_2 \xrightarrow{(b)} CH_3{-}\dot{C}H{-}\underset{Br}{\underset{|}{CH_2}}$$

Propylene — 2° Free radical (more stable)

The order of stability of free radicals is 3° > 2° > 1°. Therefore, the more stable 2° free radical is formed predominantly.

Step 4. More stable 2° free radical attacks the H—Br molecule to form *anti*-Markovnikov product and a bromine atom. The bromine atom goes back to step 3.

$$CH_3{-}\dot{C}H{-}CH_2Br + H : Br \longrightarrow CH_3{-}CH_2{-}CH_2Br + Br\cdot$$

n-Propyl bromide

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Thank You