



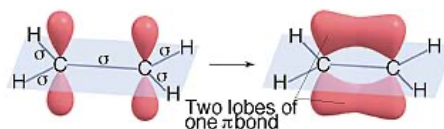
REACTIONS OF ALKENES 1

ELECTROPHILIC ADDITION

Alkenes are susceptible to attack by **electrophiles** (lone pair acceptors).

This is because the C=C double bond is very electron rich due to the electron cloud of the π bond.

In an **addition** reaction, the C=C double bond opens up and an atom or group of atoms joins onto each C of the C=C double bond.



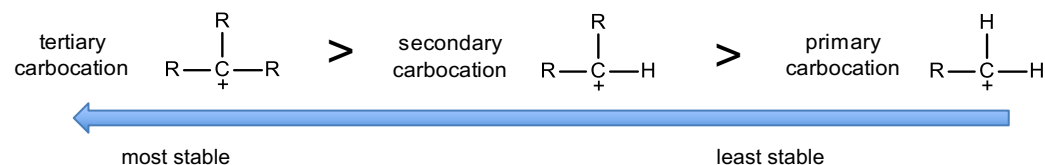
Carbocation intermediates

During the reaction, a **carbocation** is formed as an intermediate species in the mechanism.

Cations are positive ions (anions are negative ions).

Positive ions with the positive charge on the C atom are called **carbocations**.

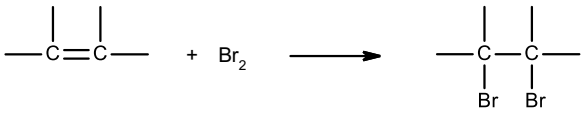
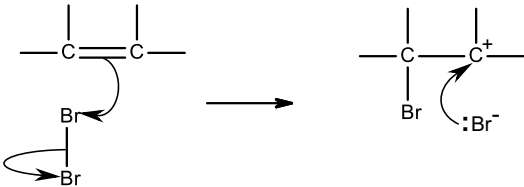
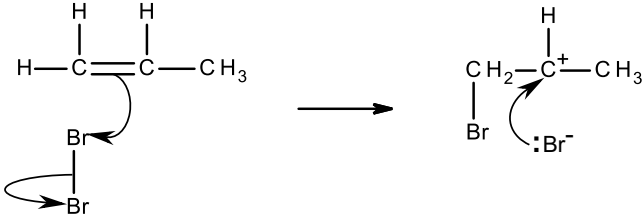
Carbocations are very unstable as the C atom only has 6 electrons around it in the outer shell. In terms of stability, tertiary carbocations (which have three alkyl groups bonded to the C⁺ atom) are the most stable (or least unstable).



Alkyl groups (e.g. methyl, ethyl, etc) are electron-releasing compared to hydrogen atoms (this is called the **inductive effect**). Therefore the more alkyl groups (rather than H atoms) on the C⁺ atom, the more stable the carbocation. This explains why in terms of stability $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$ carbocations.

When alkenes undergo electrophilic addition reactions and different carbocations can be formed, the main product formed will be from the **more stable carbocation intermediate**. It is the structure and so stability of the carbocation intermediate that matters (not the structure / stability of the product).

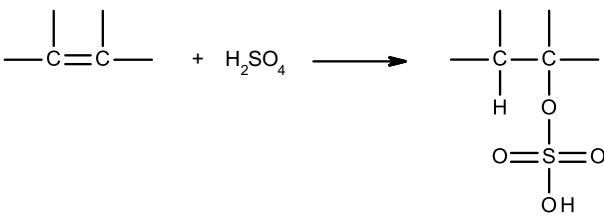
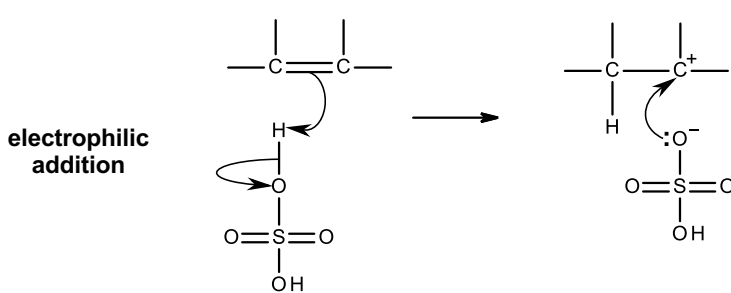
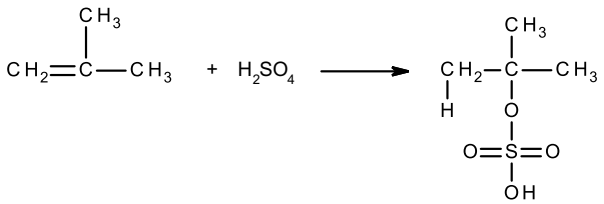
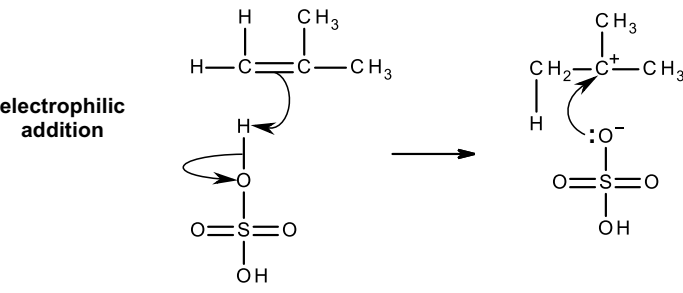
ELECTROPHILIC ADDITION 1 – reaction with Br₂

Reagent	Br ₂
Conditions	aqueous (i.e. bromine water)
What happens	C=C opens up; and added onto the two C atoms of the C=C double bond are: Br & Br
Overall equation	
Mechanism	electrophilic addition 
Example 1	e.g. propene + Br₂ $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{Br}_2 \longrightarrow \begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \\ \text{Br} \quad \text{Br} \end{array}$ electrophilic addition 
Example 2	e.g. but-2-ene + Br₂

ELECTROPHILIC ADDITION 2 – reaction with HBr

Reagent	HBr
Conditions	
What happens	C=C opens up; and added onto the two C atoms of the C=C double bond are: H & Br
Overall equation	$\text{>C=C<} + \text{HBr} \longrightarrow \begin{array}{c} \text{>C}-\text{C<} \\ \quad \\ \text{H} \quad \text{Br} \end{array}$
Mechanism	electrophilic addition
Example 3	e.g. propene + HBr $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{HBr} \longrightarrow \begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \\ \text{H} \quad \text{Br} \end{array}$ electrophilic addition The main product is 2-bromopropane which is formed: - from the 2^y carbocation intermediate $\text{CH}_3\text{C}^+\text{HCH}_3$ rather than the alternative 1^y carbocation intermediate $\text{CH}_3\text{CH}_2\text{C}^+\text{H}_2$ - the 2^y carbocation intermediate is more stable than the 1^y due to the inductive effect of two alkyl groups rather than one alkyl group.
Example 4	e.g. methylpropene + HBr

ELECTROPHILIC ADDITION 3 – reaction with H₂SO₄

Reagent	H ₂ SO ₄
Conditions	Concentrated H ₂ SO ₄ , cold (typically at room temperature)
What happens	C=C opens up; and added onto the two C atoms of the C=C double bond are: H & O-SO ₂ OH
Overall equation	
Mechanism	
Example 5	e.g. methylpropene + conc H₂SO₄  electrophilic addition  The main product is is formed: - from the 3^y carbocation intermediate (CH₃)₃C⁺ rather than the alternative 1^y carbocation intermediate (CH₃)₂CHC⁺H₂ - the 3^y carbocation intermediate is more stable than the 1^y due to the inductive effect of three alkyl groups rather than one alkyl group.

Example 5	e.g. but-1-ene + conc H ₂ SO ₄
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ELECTROPHILIC ADDITION 4 – reaction with H₂O

Reagent	H ₂ O with strong acid (e.g. H ₂ SO ₄ , H ₃ PO ₄)
Conditions	
What happens	C=C opens up; and added onto the two C atoms of the C=C double bond are: H & OH
Overall equation	$\text{---C=C---} + \text{H}_2\text{O} \longrightarrow \begin{array}{c} \text{---C---C---} \\ \quad \\ \text{H} \quad \text{OH} \end{array}$
Mechanism	electrophilic addition
Example 7	e.g. propene + water (in presence of strong acid catalyst) $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{H}_2\text{O} \longrightarrow \begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \\ \text{H} \quad \text{OH} \end{array}$ electrophilic addition The main product is formed: - from the 2^o carbocation intermediate CH₃C⁺HCH₃ rather than the alternative 1^o carbocation intermediate CH₃CH₂C⁺H₂ - the 2^o carbocation intermediate is more stable than the 1^o due to the inductive effect of two alkyl groups rather than one alkyl group.
Example 8	e.g. but-2-ene + water (in presence of strong acid catalyst)