

Can be electrophilic, nucleophilic, homolytic, heterolytic, cyclic...

**Electrophilic Addition of Bromine to alkene** 



## **Mechanistic evidences**

1. The rxn is highly stereospecific with anti-addition mech.



2. Reaction rate increases with electron density of the double bond



Sum of all four  $\sigma$  \* of the substituents

additive contribution, implying symmetrical distribution of charge over the two carbon atoms in T.S.

Reaction rate decreases with e-withdrawing group.







NMR  $\delta$  2.8 singlet

NMR 3.0, 3.2 two peaks. no symmetrical structure

5. Isolation of bromonium salt



The actual mechanism is complicated, depending on structure of the alkene, solvent, temperature.



with a stabilized carbonium, the bromonium ion mech. is less important.

## Addition of HX to alkene x + x + x + x x + x x + x x + x x + x x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x + x

The reaction is usually regioselective, interpreted by the stability of carbocation formed after electrophilic attack by HX

 $\rightarrow$  Markovnikov's Rule.

The kinetics of the add'n is more complicated, depending on the substrate structure, solvent, temperature, etc...

The stereochemistry of HX add'n is predominantly anti, but





Rearragement implied involvement of carbocation



The add'n of HBr is complicated by radical rxn, which generates anti-Markovnikov product<sub>Br</sub>



Interpretation of anti-Markovnikov rule Stability of radical  $\rightarrow$  if a late T.S. is involved The radical attachment is highly exothermic  $\rightarrow$  suggesting early T.S. orientation of the addition of Br  $\cdot$  could be steric effect



## **Epoxidation**



Electrophilic rxn : rate increase with e-donating gp on olefin and e-withdrawing group on  $\underline{R}CO_3H$ 

Second order

rate = *k*[Alkene][peracid]



symmetrical



unsymmetrical T.S.