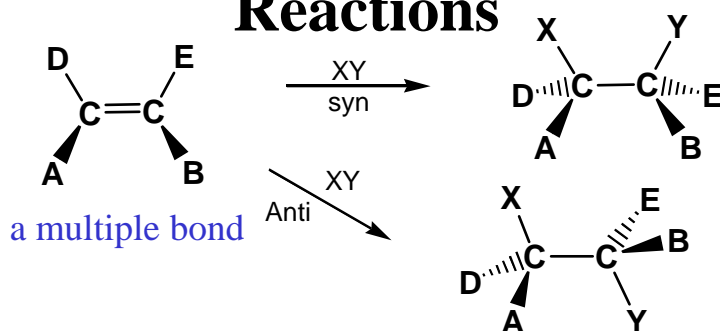


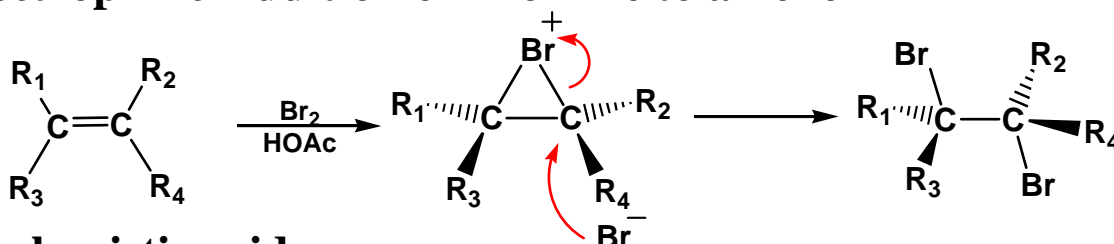
Chap. 9 Addition

Reactions



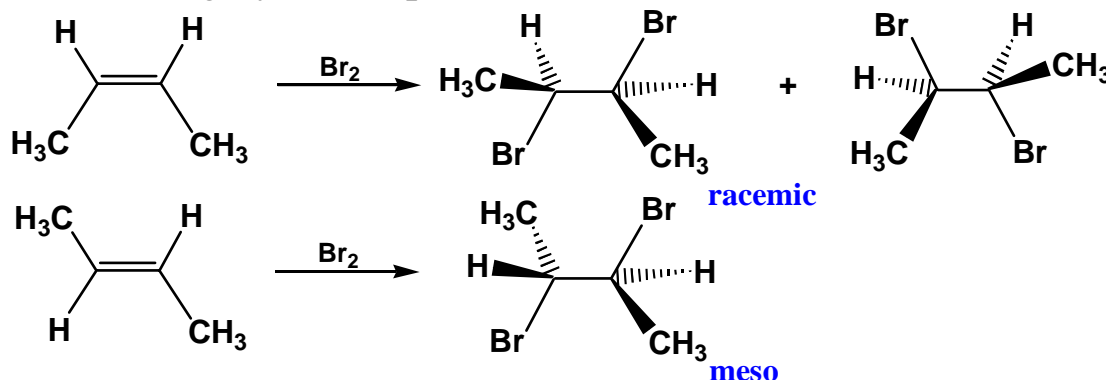
Can be electrophilic, nucleophilic, homolytic, heterolytic, cyclic...

Electrophilic Addition of Bromine to alkene

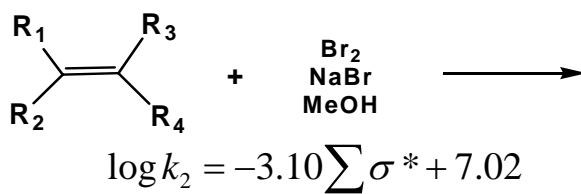


Mechanistic evidences

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

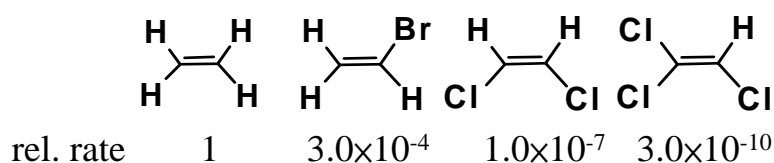


2. Reaction rate increases with electron density of the double bond

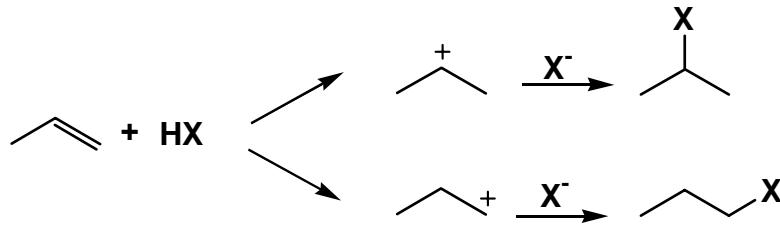


Sum of all four σ^* of the substituents additive contribution, implying symmetrical distribution of charge over the two carbon atoms in T.S.

Reaction rate decreases with e-withdrawing group.



Addition of HX to alkene



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

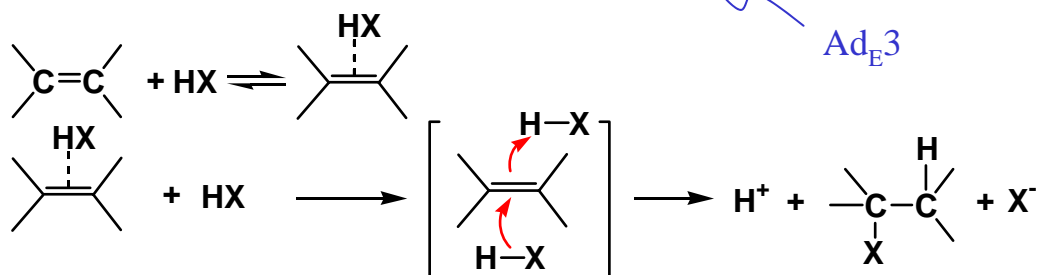
→ Markovnikov's Rule.

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

e.g. add'n of HCl to , , ...

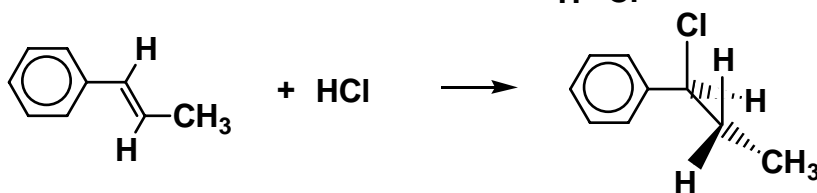
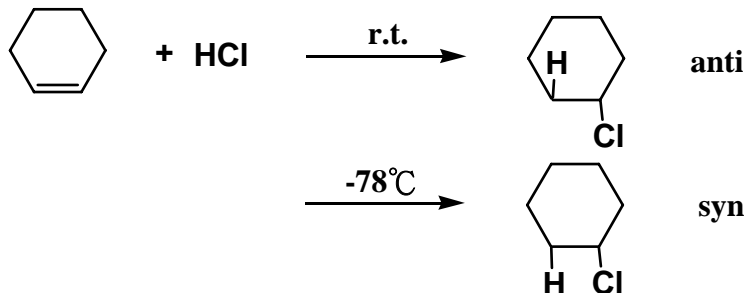
HBr to

$$\text{rate} = k[\text{alkene}][\text{HX}]^2$$



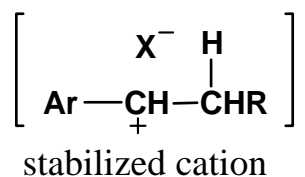
The stereochemistry of HX add'n is predominantly anti,

but

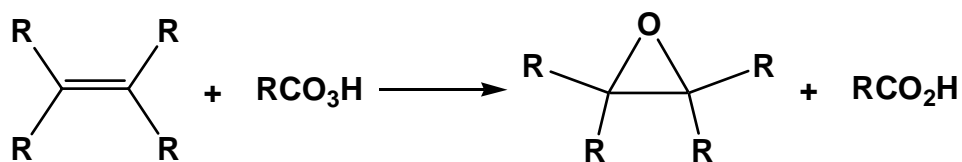


$$\text{rate} = k[\text{alkene}][\text{HCl}]$$

syn (through ion pair)

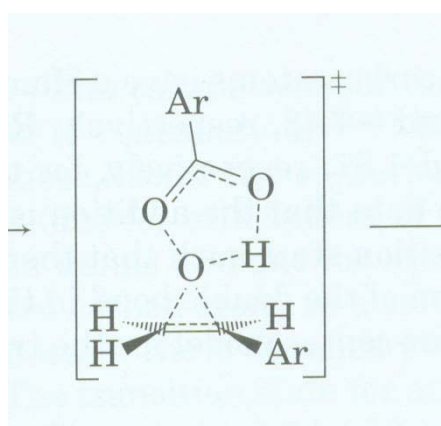


Epoxidation

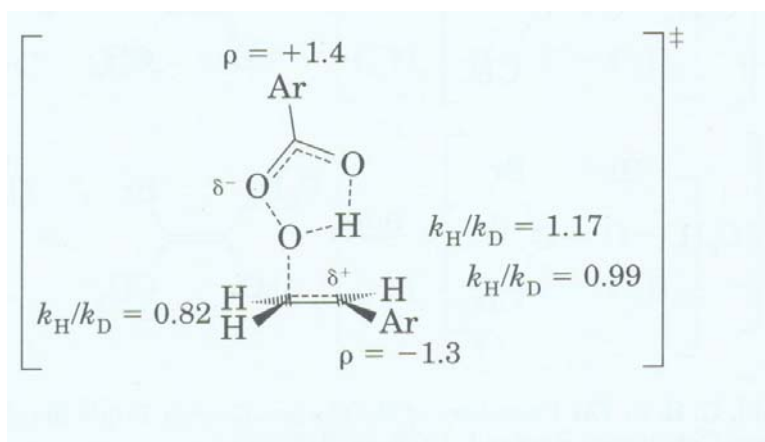


Electrophilic rxn : rate increase with e-donating gp on olefin and e-withdrawing group on RCO₃H

Second order rate = $k[\text{Alkene}][\text{peracid}]$



symmetrical



unsymmetrical
T.S.