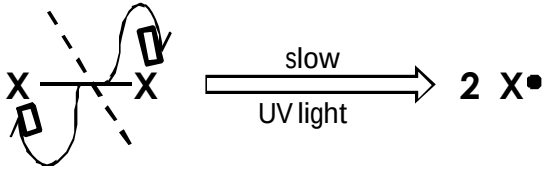
Free Radical Chain Reaction: Alkane + Halogen

1) Initiation: photochemical homolysis *RDS*

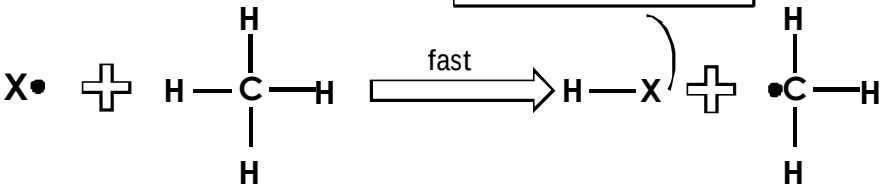


- Halogen free radicals

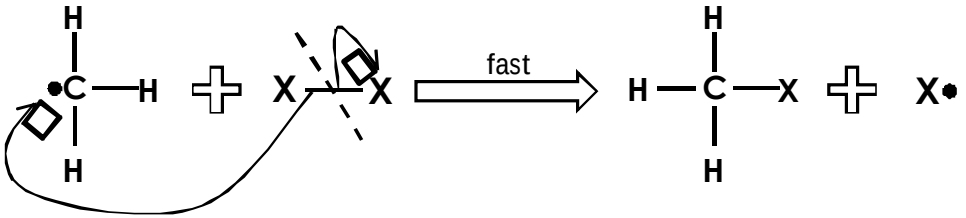
Homolytic fission - electron pair splits to form two free radicals

2) Propagation

Bond stability depends on size of atom

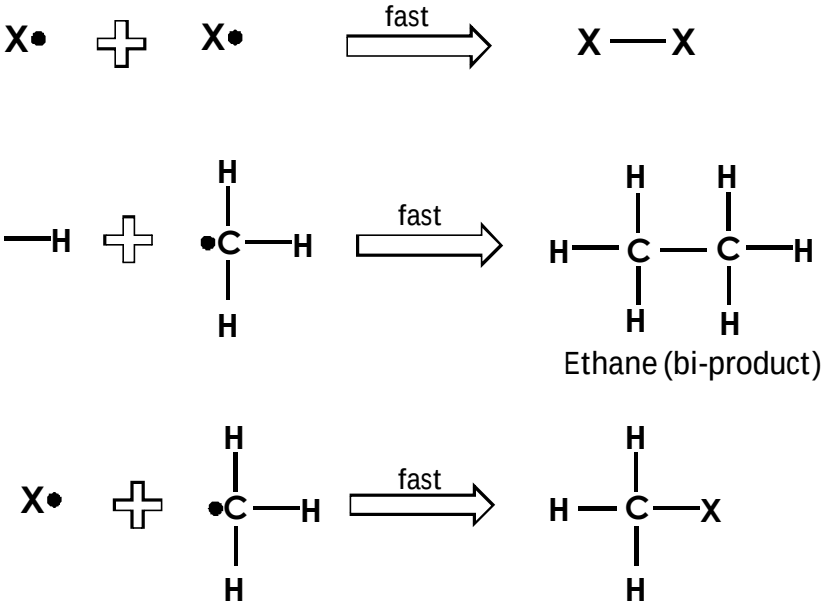


- Methyl free radical

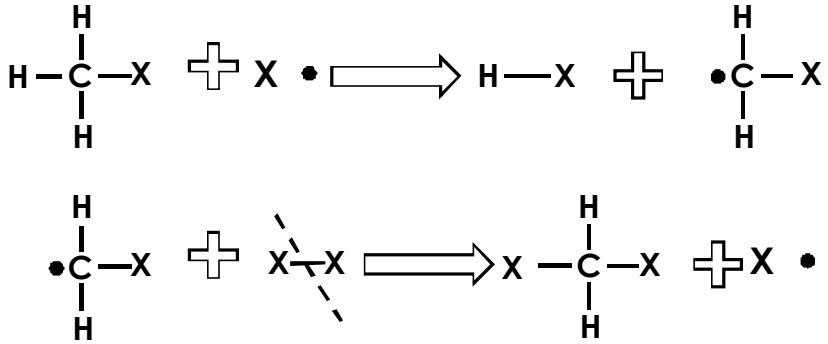


3) Termination

Reaction comes to a stop if 2 free radicals pair up



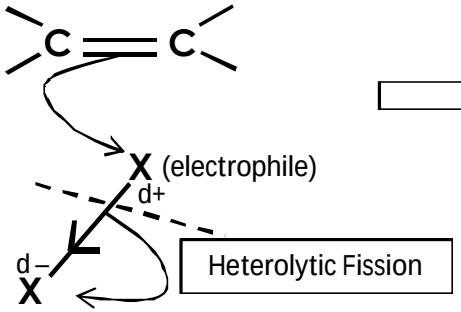
Additional halogens can add on during propagation...



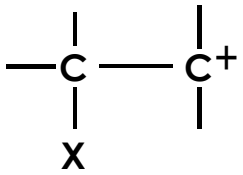
Further reaction will result in the substitution of all hydrogens with halogens

Electrophilic Addition: Alkene + Halogen

Halogen approaches alkene:



slow



Carbocation

Anion (nucleophile) will attack carbocation through backside attack

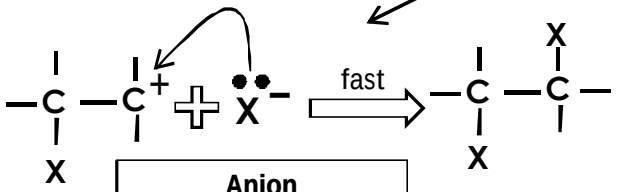
Anion depends on solution

- Dipole induced
- Bond lengthens and weakens

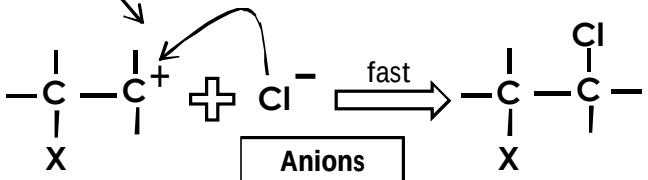
Inert solution

Dissolved in water

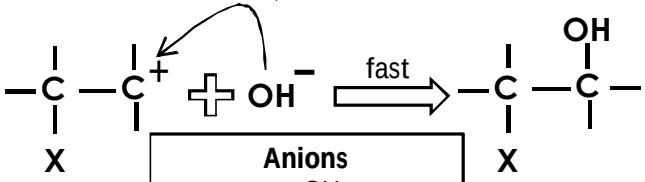
Dissolved in NaCl



Anion
- X^- (halide anion)



Anions
- Cl^-
- X^-



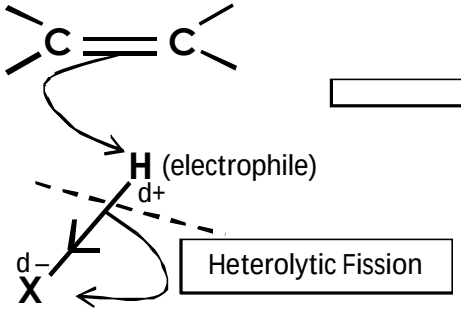
Anions
- OH^-
- X^-

Example - Bromine and Ethene ($X = Br_2$)

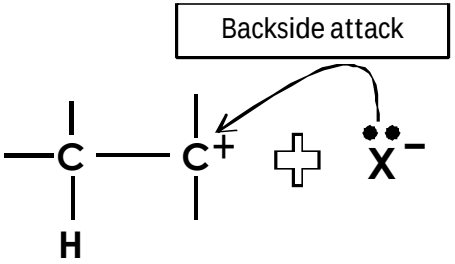
Inert Solution:	1,2 – dibromoethane
Bromine Dissolved in Water:	2-bromo ethan-1-ol
Bromine Dissolved in NaCl:	1-bromo, 2-chloro ethane

Electrophilic Addition: Alkene + Hydrogen Halide

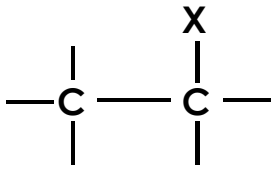
Hydrogen Halide approaches alkene



slow

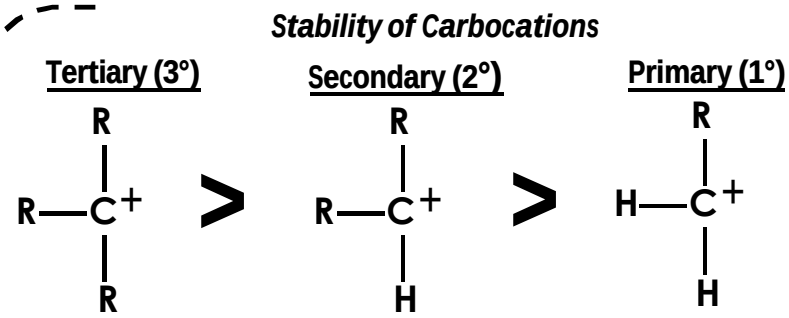


fast



- Existing dipole strengthened
- Bond lengthens and weakens

Stability of Carbocations



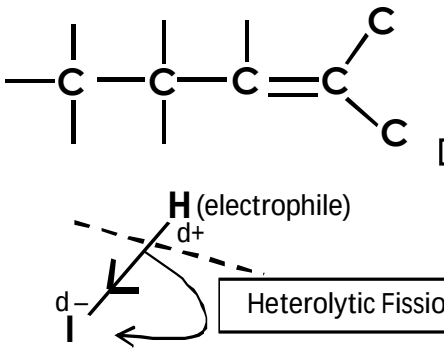
*Positive inductive effect : alkyl groups donate electron density to centre carbon

-Carbon with the most electron density is the most stable

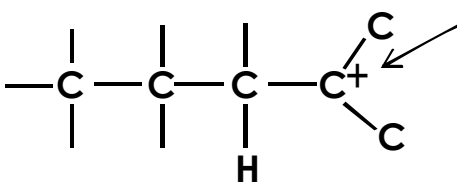
Note: for asymmetric alkenes, ***Markovnikov's rule*** is used

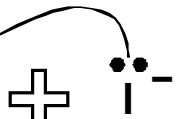
- Hydrogen will bond to the carbon richest in hydrogens
  -This allows for the most stable carbocation to form
- Hydrogen will be abstracted from the Carbon atom bonded to the least hydrogen atoms
- Tend to create alkyl groups, not destroy them

Example – Hydrogen iodide and 2-methyl pent-2-ene(X = I_2)

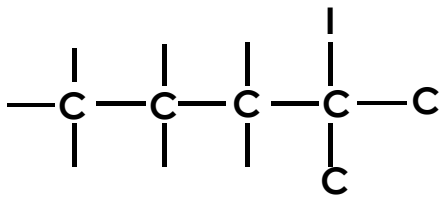


slow

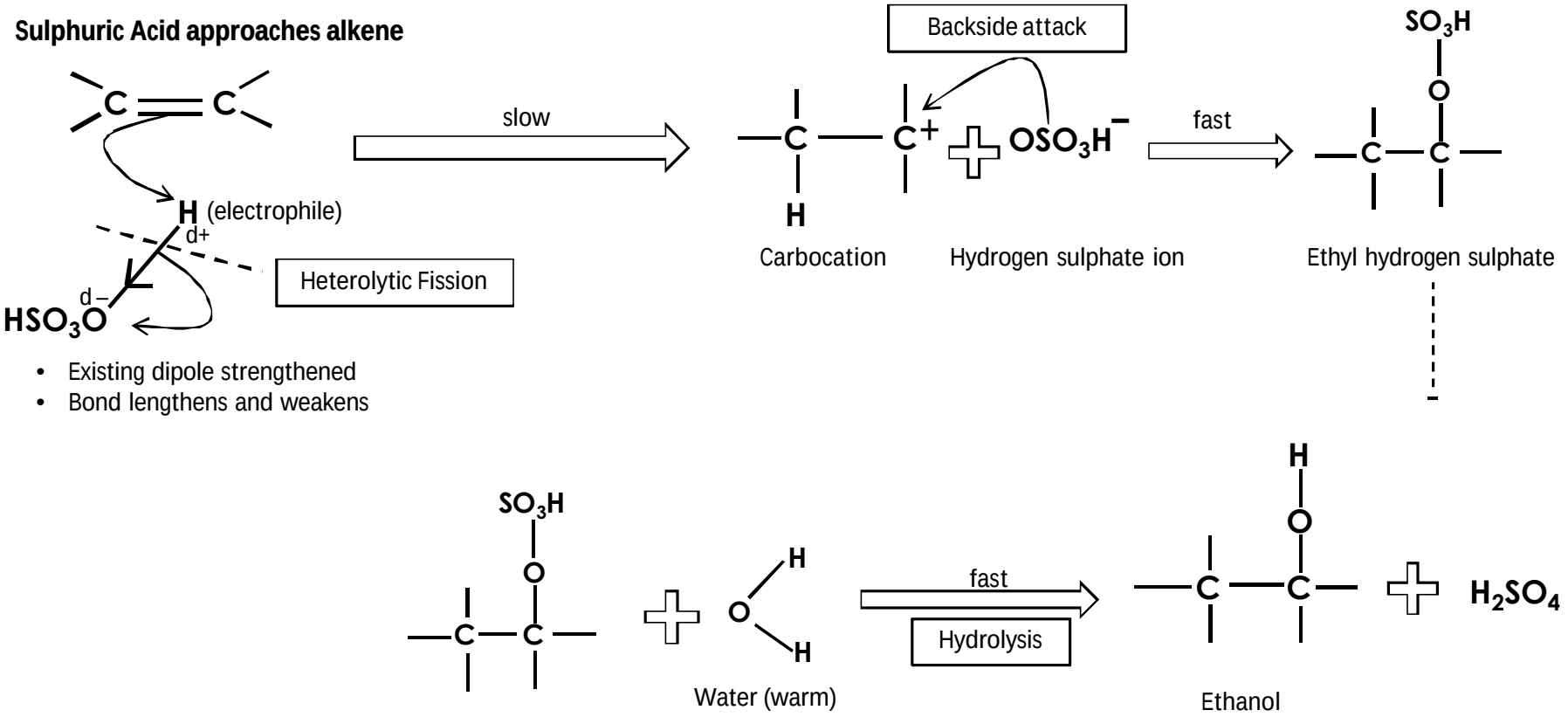




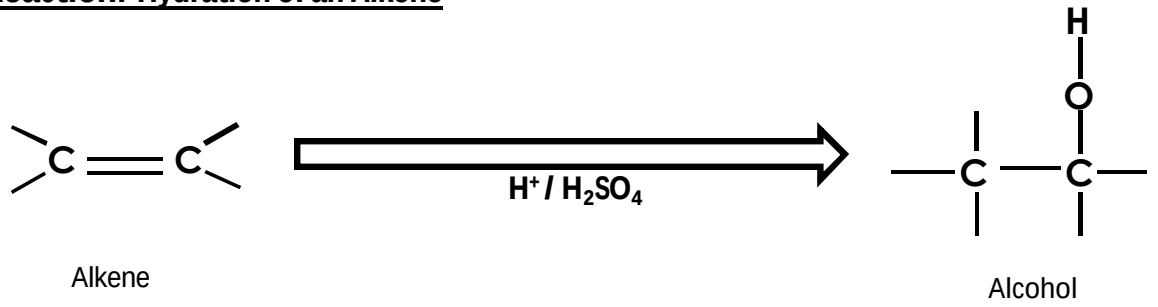
fast



Electrophilic Addition: Alkene + Conc. Sulphuric Acid (with silver catalyst) + Water



Net Reaction: Hydration of an Alkene



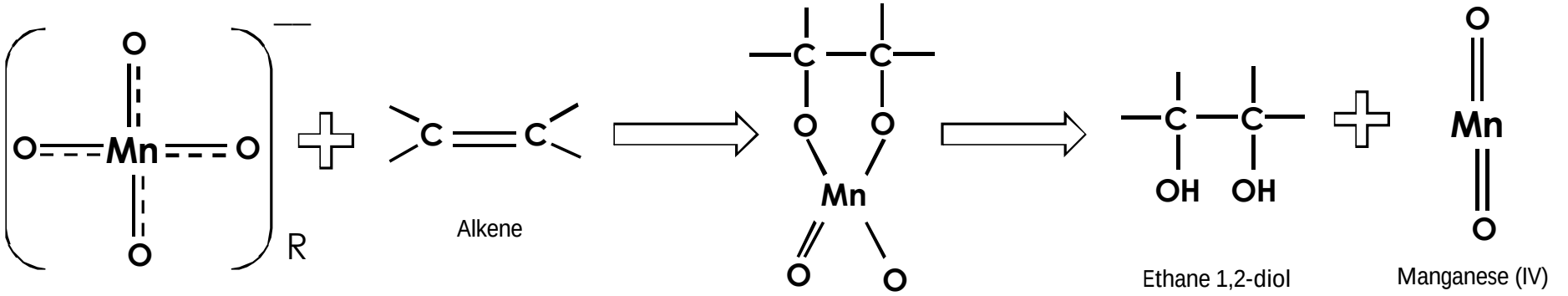
This reaction is industrially important in the preparation of alcohols

Oxidation of Alkenes: Alkene + Oxidizing Agent

Cold, dilute

Oxidizing Agent: $KMnO_4$ — MnO_4^{--}

- Potassium Permanganate
- Oxidizing Agent
- Permanganate ion
- Purple
- Oxid # Mn = +7

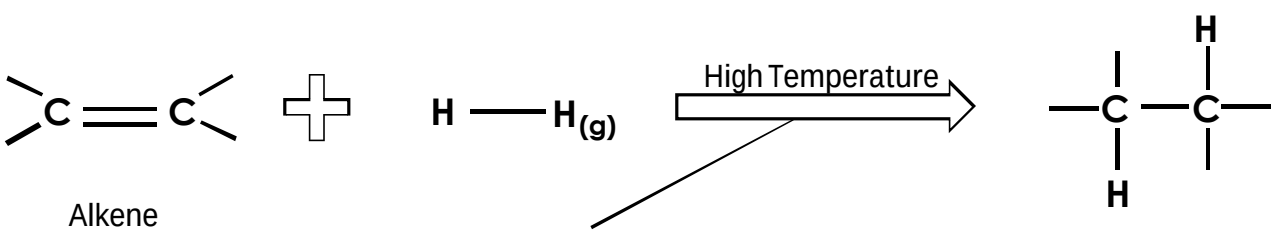


- Permanganate Ion
- Oxidizing Agent
- Purple

Transition state

- Oxid # Mn = +4

Alkene + Hydrogen : Reduction of Alkenes/ Hydrogenation

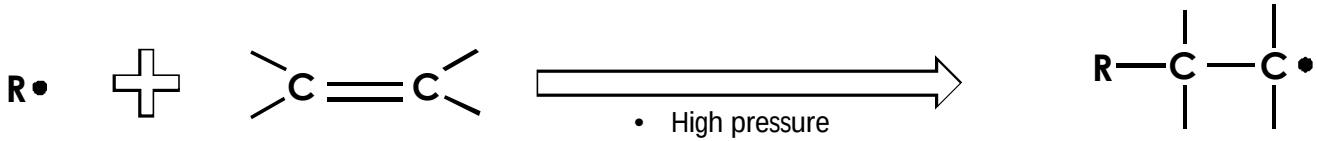


Catalyst: Transition Metal

- Pt, Ni, Pd
- Heterogeneous Catalysis
  -Absorption, reaction, desorption

This method is used in the food industry to solidify oils into edible fats (ex: margarine)

Addition Polymerization: Alkene + Free Radical

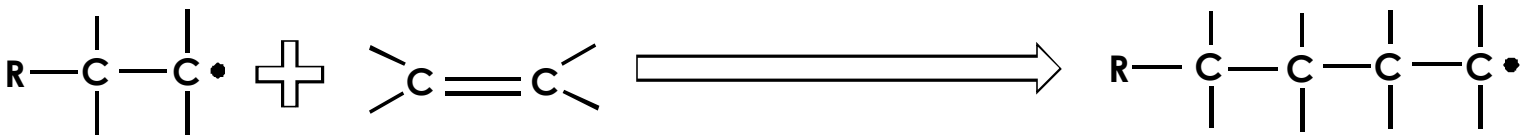


Free Radical — Alkene

- High pressure
- High temperature
- Catalyst

Alkyl free radical

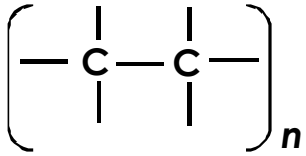
- Free radical is reproduced to continue the polymerization



Alkyl free radical — Alkene — Free radical

<u>Termination</u> occurs when 2 free radicals combine

Product:



Polyalkene

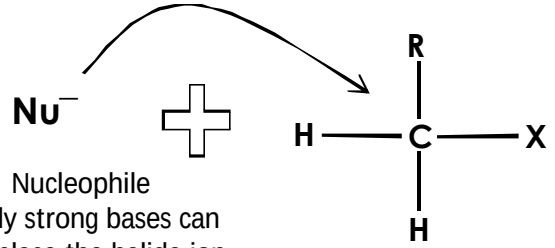
<u>Note</u>: The degree of polymerization can be altered by changing temperatures, pressures, catalysts.

This will result in many polyalkenes with a variety of different characteristics

S_N2: Haloalkane Nucleophilic Substitution

Rate Determining Step = k [R-X]^1 [Nucleophile]^1

Backside attack



Nucleophile

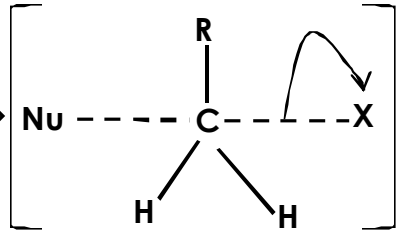
- Only strong bases can displace the halide ion (CN^-, OH^-, NH_3)

Primary Haloalkane

slow

Nonpolar solvent Low temp.

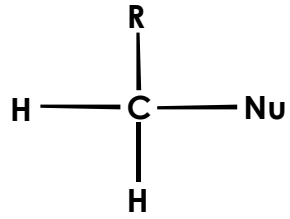
Heterolytic Fission



Transition State

- Trigonal bipyramidal
- Bonds must flatten themselves for a planar arrangement
- High Potential Energy, unstable compound

fast



- Note: Inversion of configuration
- Possibility of optical isomers

Halide Ion

Concerted reaction: everything happens all at once, there is no intermediate

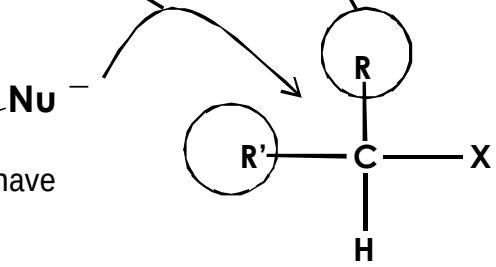
Secondary Haloalkanes will undergo SN2 when *steric hindrance* does not occur (when alkyl groups are not too large):

Effect of Steric Hindrance on Secondary Haloalkane:

Nucleophile's path is blocked

Big bulky alkyl groups

long chains/ branching



Nucleophile does not have space to attack carbon

S_N1: Haloalkane Nucleophilic Substitution

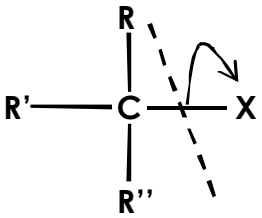
Non-concerted reaction: contains multiple steps and has an intermediate

Rate Determining Step = k [R-X]^1

Note: Polar solvents will hydrate the carbocation and stabilize it

The ion-dipole attraction provides energy for Step I

Step I :

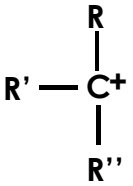


Heterolytic Fission

Tertiary Haloalkane

slow

Warm temperature
Dilute polar solvent
Alkali



Tertiary Carbocation

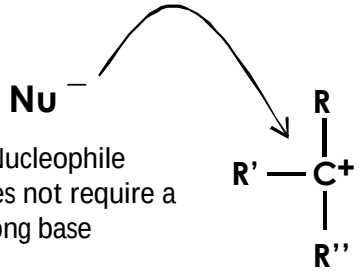
Halide Ion

- Intermediate
- Most stable due to positive inductive effect of alkyl groups
- Transient existence
- Trigonal planar , 120º, equal opportunity for nucleophile to come in from any side

Secondary Alkanes will undergo SN1 if alkyl groups are too large hence, *steric hindrance* is present

Nucleophilic Substitution

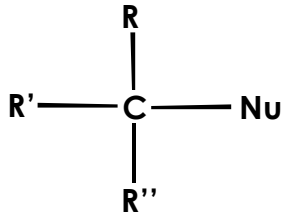
Step II:



Nucleophile

- Does not require a strong base

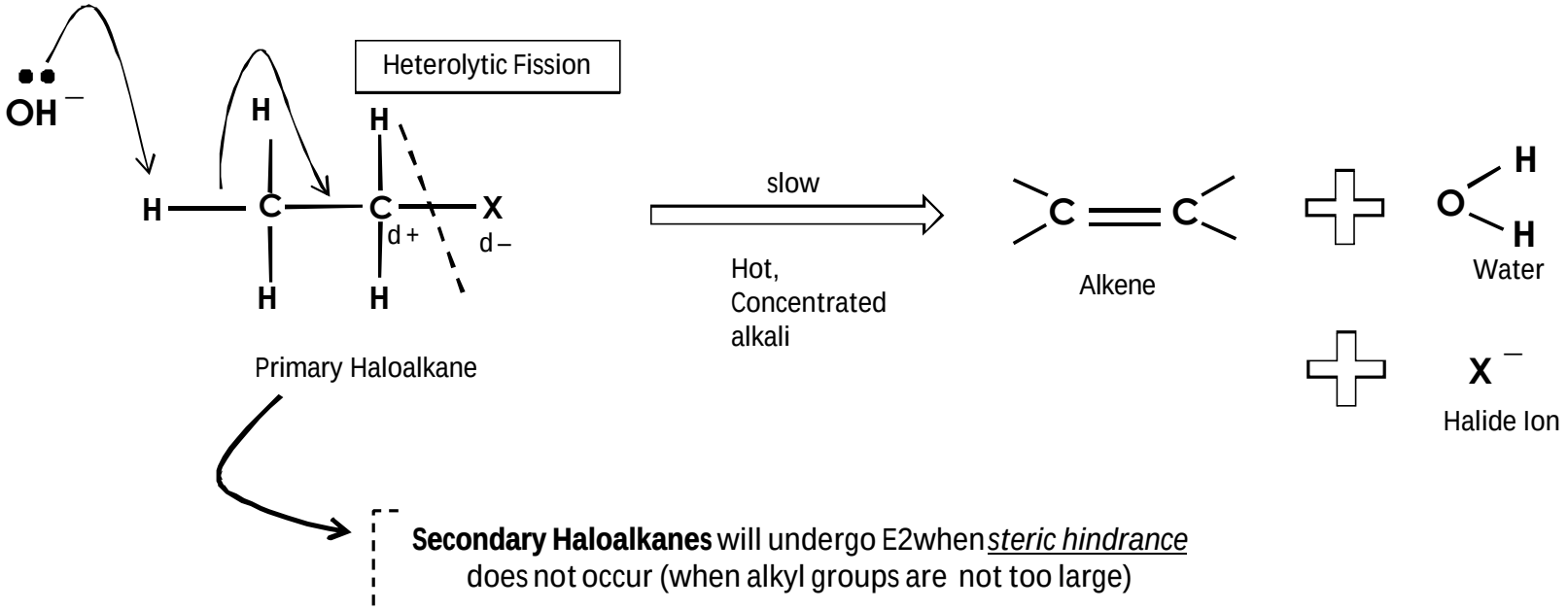
fast



Forms racemic mixture:
Products optically inactive

E2: Haloalkane Elimination Reaction

Elimination occurs instead of substitution when pathway of nucleophile is blocked, hence the Lewis base will remove an electrophile from the haloalkane instead



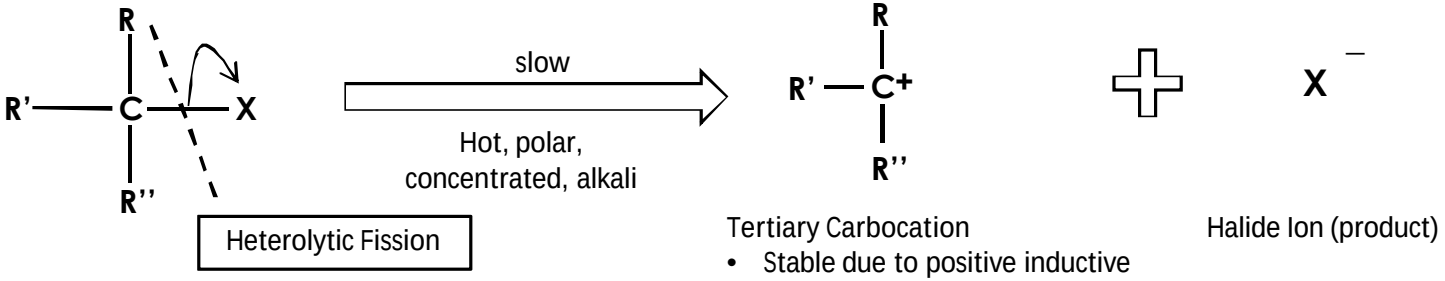
Secondary Haloalkanes will undergo E2 when *steric hindrance* does not occur (when alkyl groups are not too large)

Note: Elimination requires more energy than substitution

The elimination reaction is favoured if:
a) the base is strong
b) the temperature is high

E1: Haloalkane Elimination Reaction

Step I :



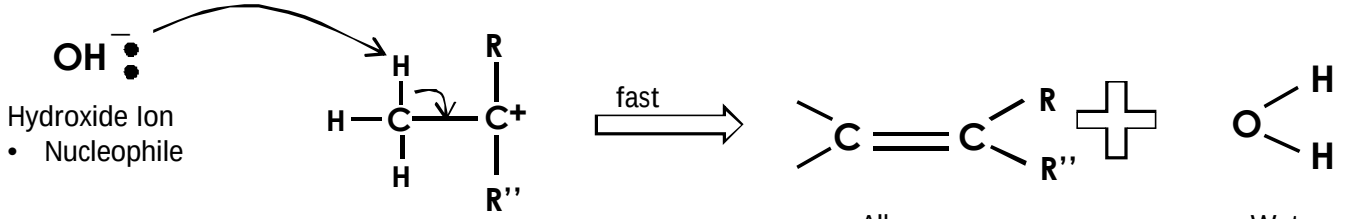
Tertiary Haloalkane

Tertiary Carbocation
- Stable due to positive inductive effect of alkyl groups
- Intermediate

Halide Ion (product)

Nucleophilic Elimination

Step II :



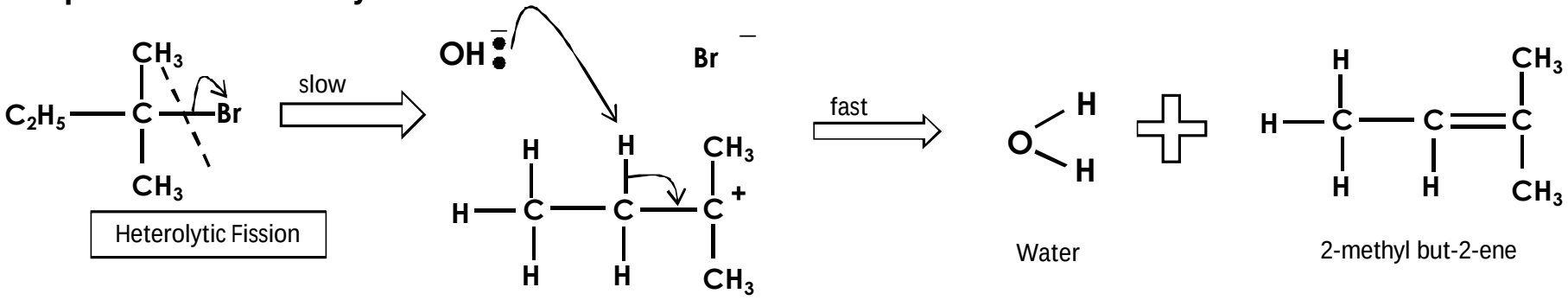
Hydroxide Ion
- Nucleophile

Alkene

Water

Note: Markovnikov's rule still applies
-When adding Hydrogen, adds to carbon that is richest in Hydrogens already
-When eliminating Hydrogen, removes from carbon that has least Hydrogens

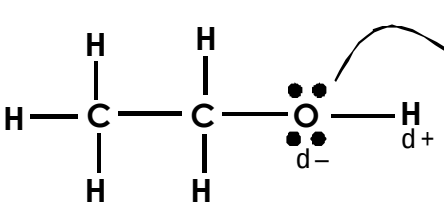
Example – 2-bromo 2-methyl butane



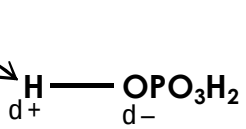
Water

2-methyl but-2-ene

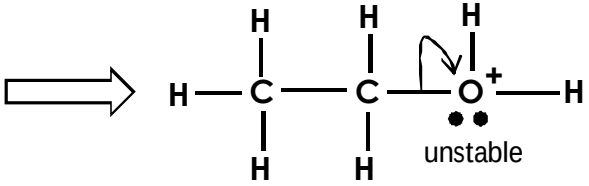
Dehydration of Alcohols: Elimination Reaction



Alcohol



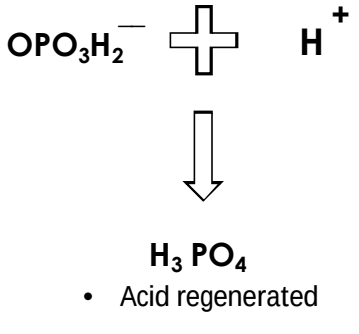
Phosphoric Acid
(dehydrating agent,
homogeneous catalyst)



unstable

Protonated Alcohol

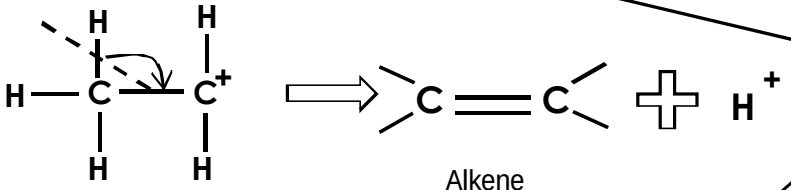
Dihydrogen Phosphate ion



H_3PO_4

- Acid regenerated

Excess Acid+ High Temperature:



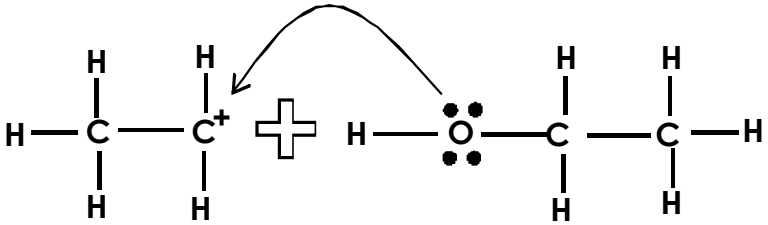
Heterolytic Fission

Alkene

Carbocation

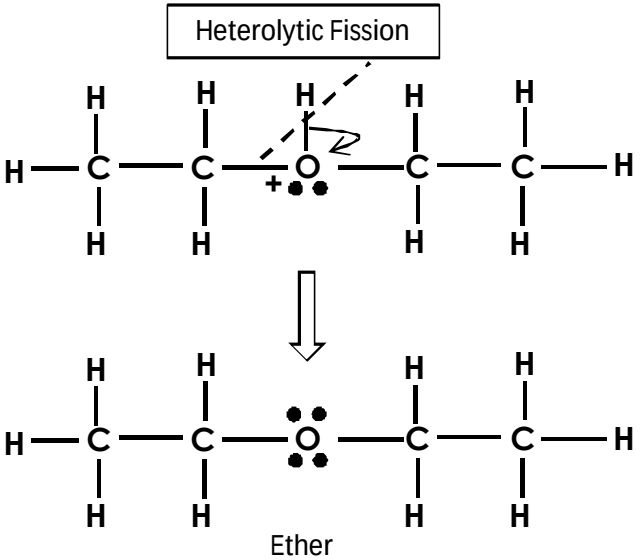
Water

Excess Alcohol + Low Temperature:



Alcohol

Heterolytic Fission



Ether

Oxidation of Alcohols: Alcohol + Oxidizing Agent

reduced

$K_2Cr_2O_7$ —— $Cr_2O_7^{2--}$ ———— $2\,Cr^{3+}$ ———— [O]

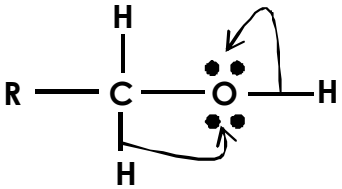
- Acidified Potassium Dichromate
- Oxidizing Agent

- Dichromate (VI) ion
- Orange
- Oxid # Cr= +6

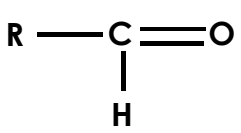
- Chromium (III) ions
- Green
- Oxid # Cr= +3

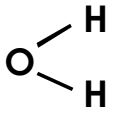
Source of Oxygen

Primary Alcohol



$H^+/Cr_2O_7^{2-}$ [O]

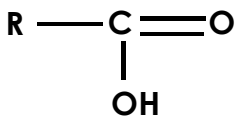




Aldehyde

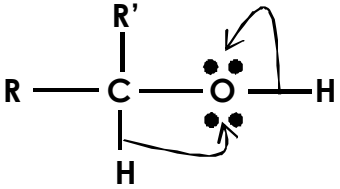
Excess Oxidizing Agent [O]

Reflux/Boil

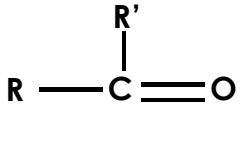


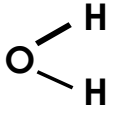
Carboxylic Acid

Secondary Alcohol



$H^+/Cr_2O_7^{2-}$ [O]



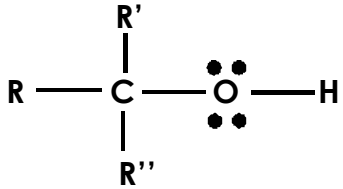


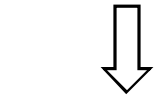
Ketone

No Oxidation Occurs

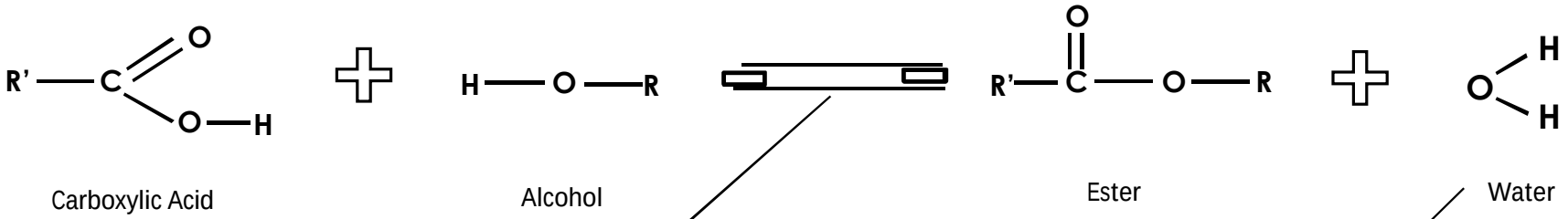
Central carbon does not have any Hydrogens to be oxidized

Tertiary Alcohol





Esterification (condensation reaction): Alcohol + Carboxylic Acid



Carboxylic Acid | Alcohol | Ester | Water

Catalyst:
concentrated sulphuric acid

- Homogeneous catalysis, participates in reaction and is regenerated afterwards
- Dehydrating agent (loss of water)
  -shifts equilibrium right, produces more product

Note: Water Is a product, not a solvent

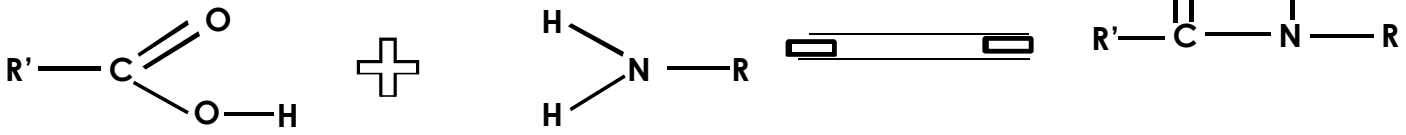
So it is included in the equilibrium calculation

$$K_c = \frac{[H_2O][Ester]}{[Alcohol][Acid]}$$

This is an example of ***condensation polymerization***:
→ A reaction in which two molecules join together to form a larger molecule with the loss of a smaller molecule

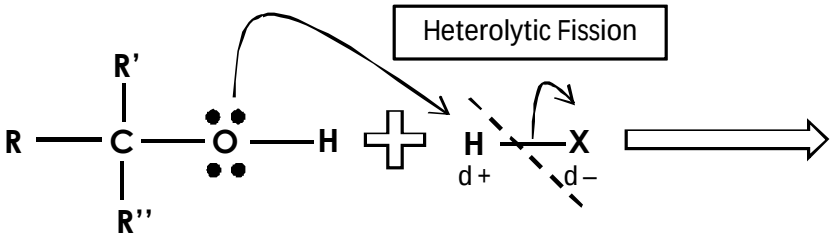
Another example of condensation polymerization is the formation of peptide linkages in proteins

Condensation Polymerization



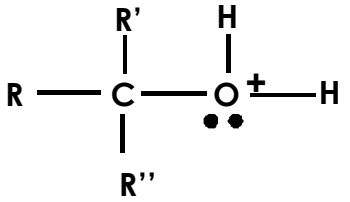
Carboxylic Acid | Amine | Peptide Linkage

Alcohol + Concentrated H-X Acid



Tertiary Alcohol
- Reacts most readily

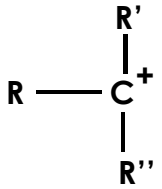
Strong Acid
- HCl
- HBr
- HI



Protonated Alcohol (intermediate)

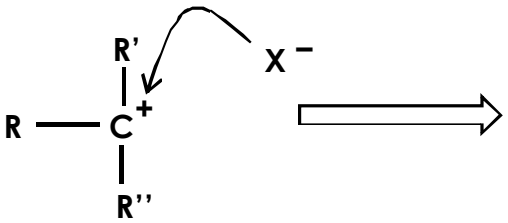
Halide ion (nucleophile)

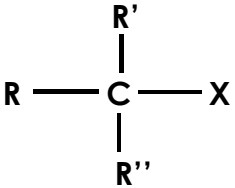
Alcohols are soluble in the concentrated halide acid
Therefore, the reactant solution is ***colourless***



Carbocation
- Tertiary carbocations are the most stable

Water





Halogenoalkane
- Useful method to prepare alkyl halides

Halogenoalkanes are not soluble in the concentrated halide acid
Therefore, the product solution is ***cloudy***

Note: This is an important test for alcohols, tertiary alcohols will react rapidly whereas primary and secondary alcohols will react more slowly or not at all

Therefore, the reaction can be used to distinguish between 1°, 2°, and 3° alcohols