CHEM 261 October 2, 2020

**Reactivity and Selectivity (Hammond Postulate)**

e.g. Halogenation of 2-methylbutane

 

+ HF

I2 does not react as above

**NOTE:**

More reactive reagents give less selective products

Less reactive reagents give more selective products

**For Exothermic Reactions**

-The transition state resembles the starting material

**For Endothermic Reactions**

-The transition state resembles the products

**Energy Diagrams for Halogenation Reactions**

*Fluorination* (ΔH < 0) *Bromination* (ΔH > 0)



small

large

TS

small

(TS similar to

SM)

large

TS

E = energy

TS = transition state

SM = starting material

**For Exothermic Reactions**

-The transition state resembles the starting material

**For Endothermic Reactions**

-The transition state resembles the products

**Reactivity TREND:**

F2 > Cl2 > Br2 >> I2  Iodine does not react



ΔH = -35 kcal/mole

Exothermic



ΔH = +16 kcal/mole

Endothermic

**Selectivity TREND:**



Bromine atom “searches” the molecule to create the most stable radical

Fluorine atom is small and feels the loss of an electron much more than bromine

* Fluorine is less precise and reacts immediately