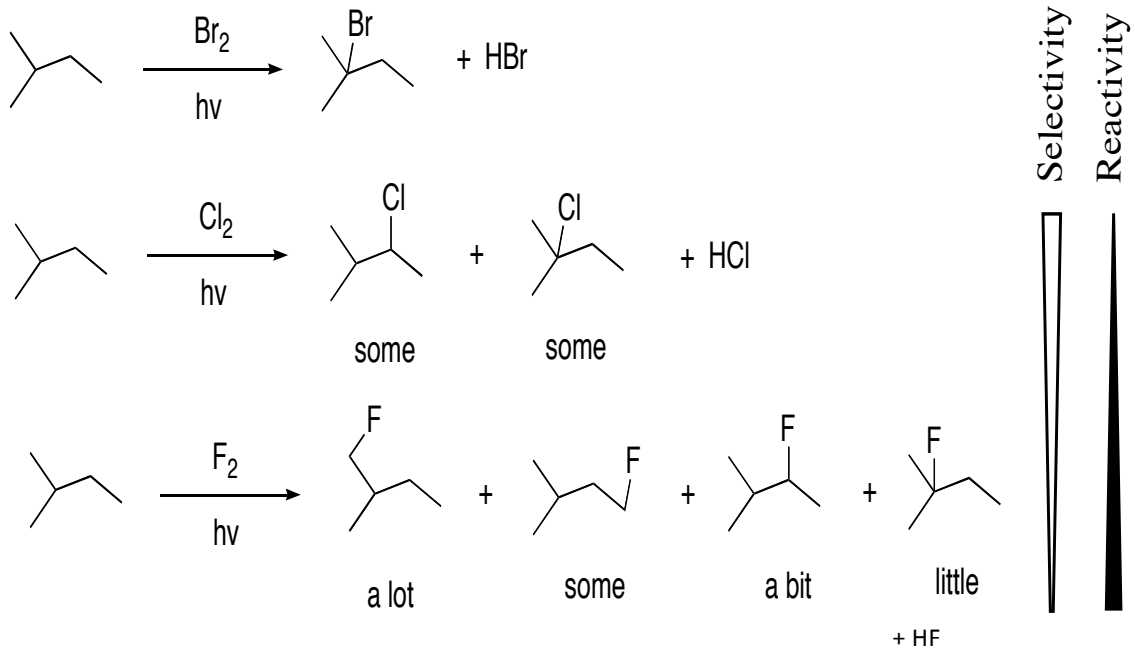
**Reactivity and Selectivity (Hammond Postulate)**

e.g. Halogenation of 2-methylbutane




$I_2$ does not react as above

**NOTE:**

More reactive reagents give less selective products
Less reactive reagents give more selective products

**For Exothermic Reactions**

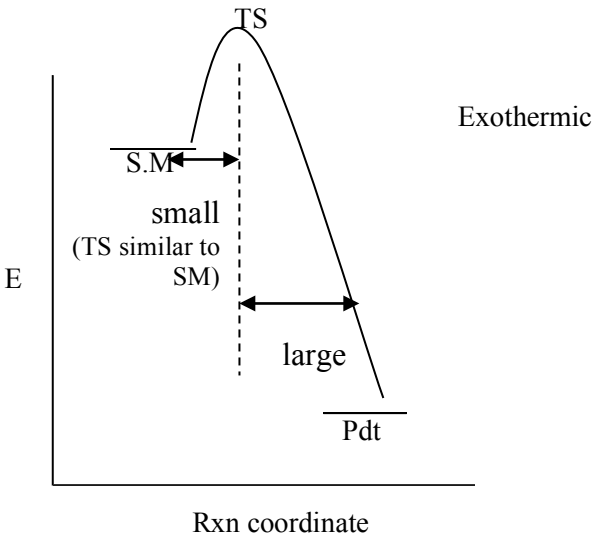
-The transition state resembles the starting material

**For Endothermic Reactions**

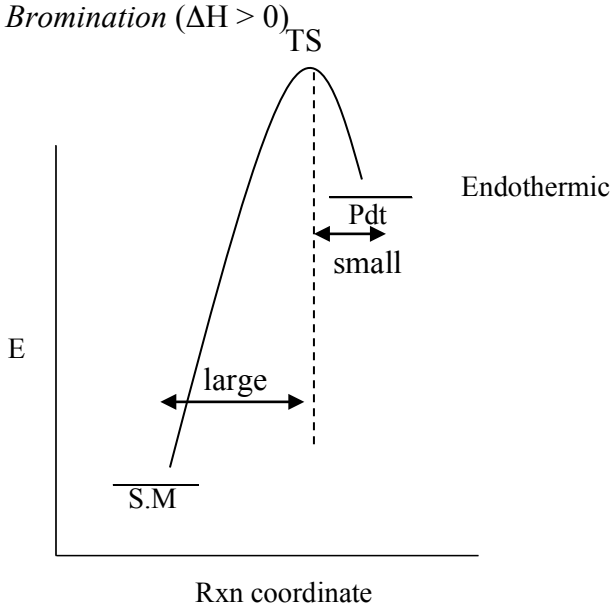
-The transition state resembles the products

**Energy Diagrams for Halogenation Reactions**

*Fluorination* ($\Delta H < 0$)




*Bromination* ($\Delta H > 0$)




E = energy
TS = transition state
SM = starting material

**For Exothermic Reactions**

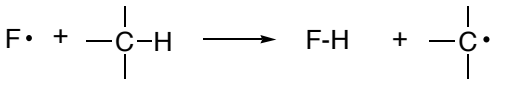
-The transition state resembles the starting material

**For Endothermic Reactions**

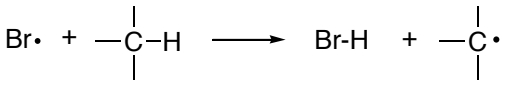
-The transition state resembles the products

**Reactivity TREND:**

$F_2 > Cl_2 > Br_2 >> I_2$ Iodine does not react



ΔH = -35 kcal/mole
Exothermic



ΔH = +16 kcal/mole
Endothermic

**Selectivity TREND:**

Br• > Cl• > F•

| most selective | least selective |
|---|---|
| endothermic | exothermic |

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