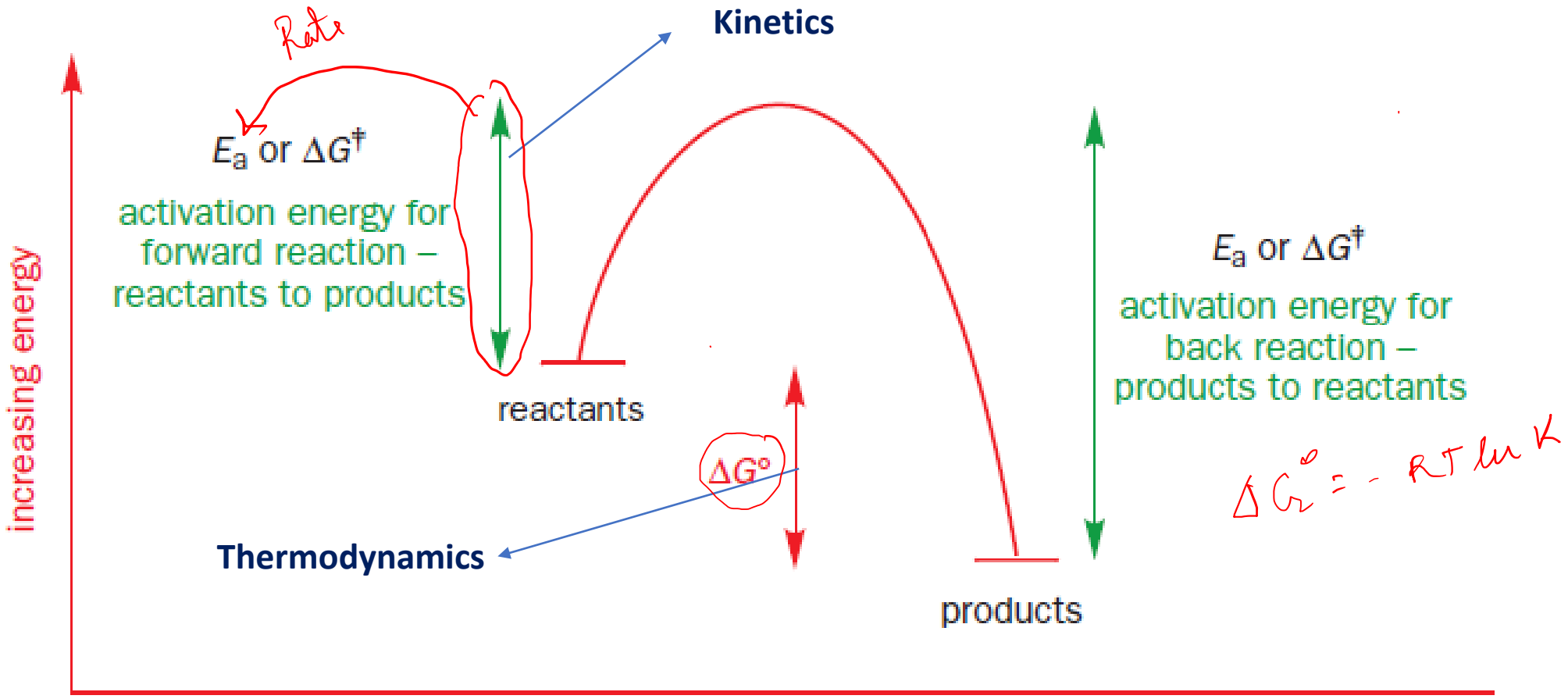
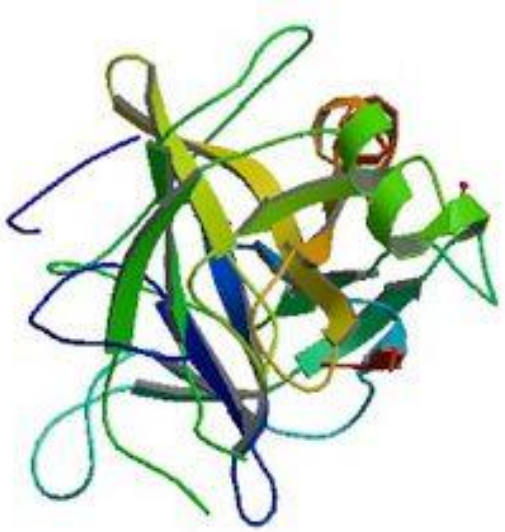
- ***Study Material for the classes on S_N1 and S_N2: Chapter-Nucleophilic Substitution at Saturated Carbon (Clayden Warren)***
- ***I will also provide a classnote***

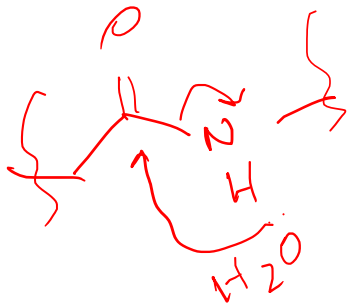


- ✓ The lower the value of E_a, the faster the reaction: Kinetically favourable
- ✓ Higher negative value of ΔG: Thermodynamically favourable

- ✓ Chymotrypsin is a digestive enzyme present in pancreatic juice
- ✓ It helps in hydrolysing peptide bonds
- ✓ These reactions are thermodynamically favorable, *but occurs extremely slowly in the absence of a catalyst*



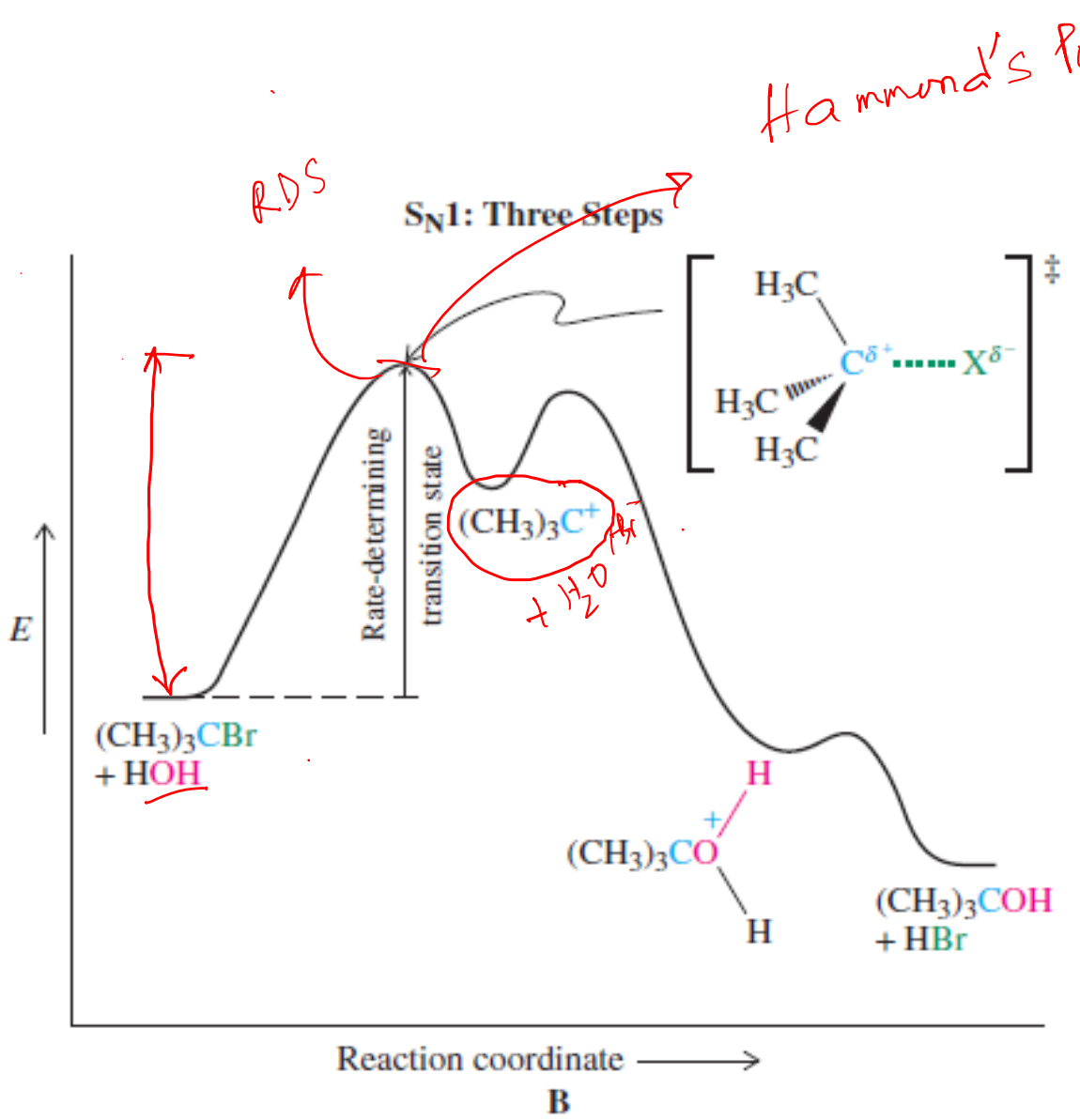
Chymotrypsin

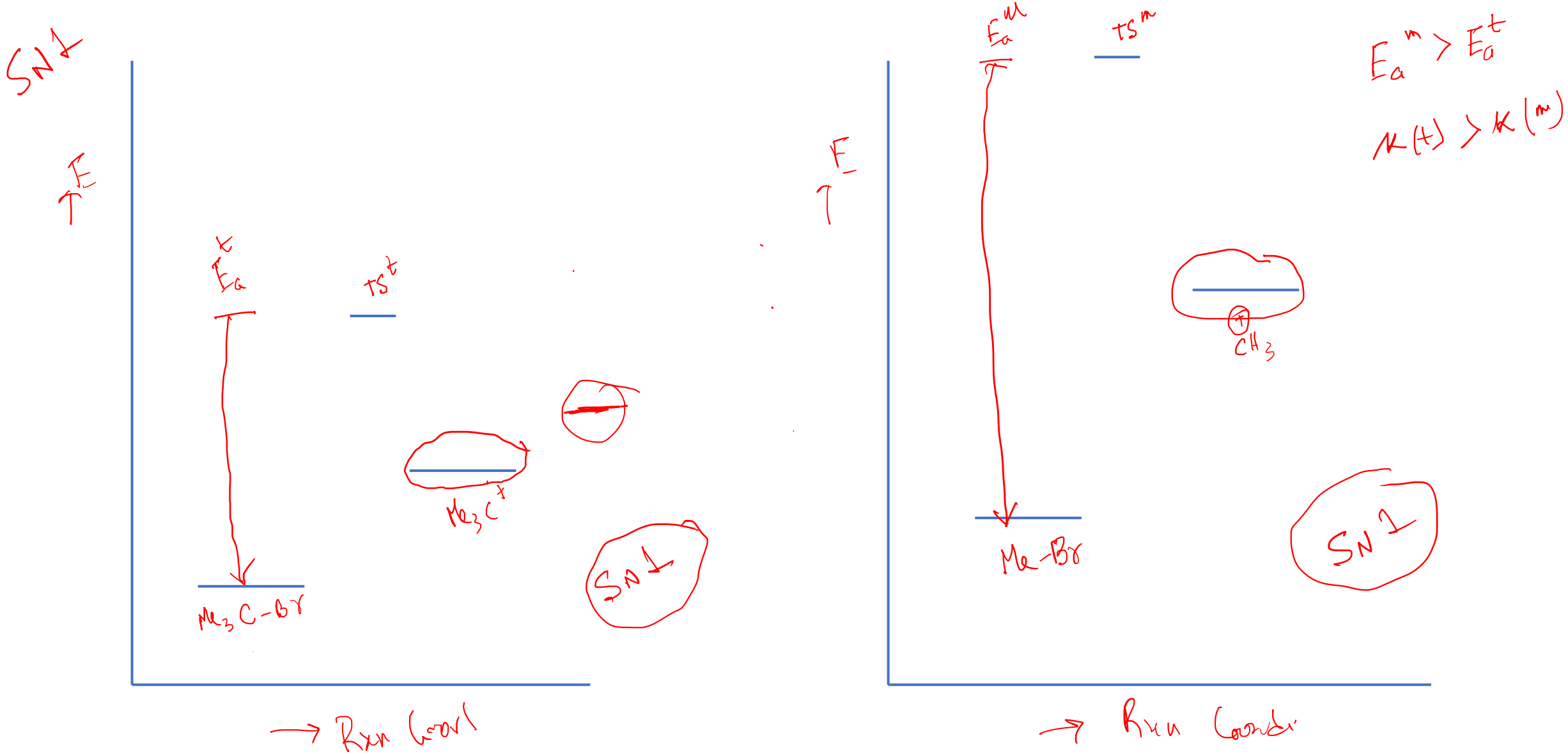


$H_2O + (CH_3)_3C\text{-}Br \longrightarrow HBr + (CH_3)_3C\text{-}OH$

Rate = k [RX]

- ✓ It is true that a t-butyl carbocation is more stable than methyl or primary carbocations
- ✓ At the same time, the activation energy of its formation (E_a) is smaller than methyl/primary: *Important for S_N1 reactions*

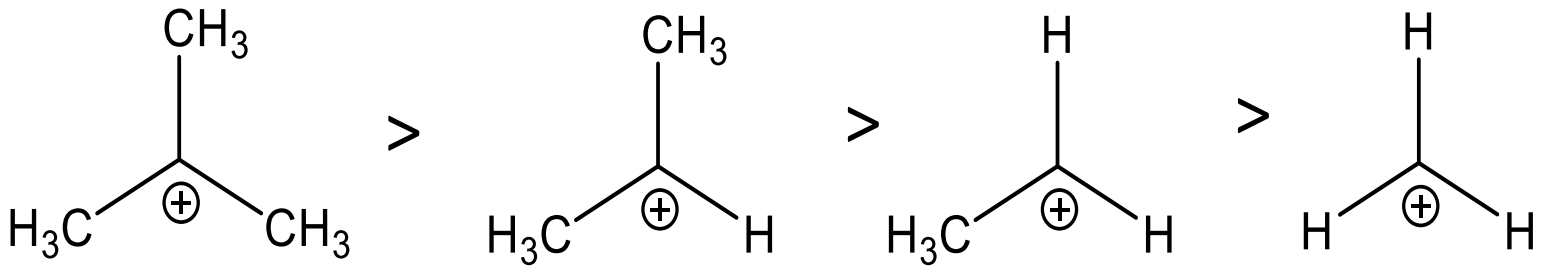




Important: *It is the lower activation energy of the formation of t-butyl cation that drives its S_N1 reaction*, not its higher thermodynamic stability compared to methyl or primary carbocations

Relative Stability of Carbocations

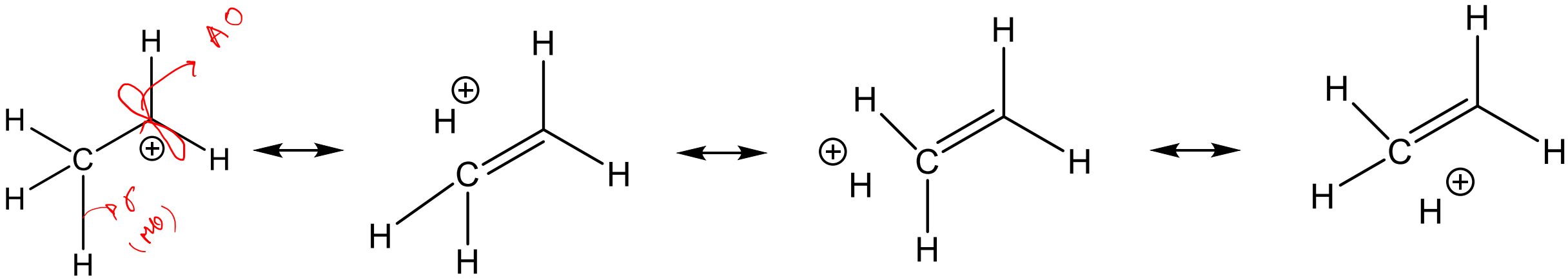
➢ The stability of the tertiary, secondary, primary and methyl carbocations follows the order:



Tertiary Secondary Primary Methyl

✓ This is generally explained by the +I effect of the -CH_3 groups

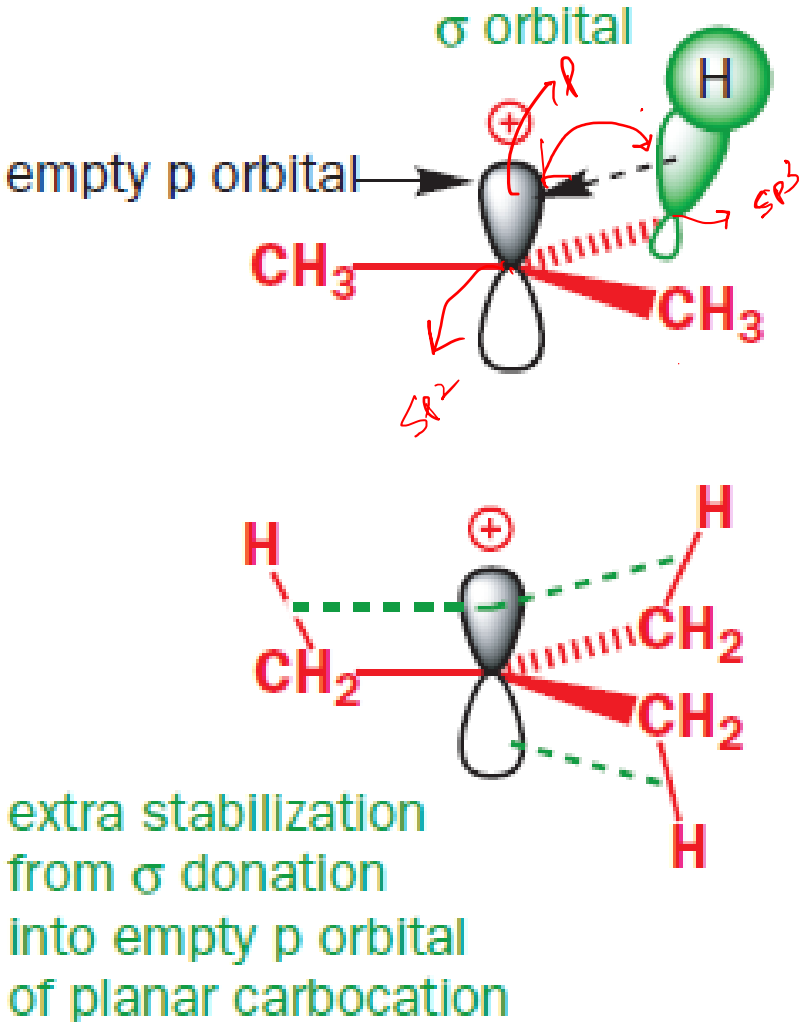
➢ However, there is another effect called *Hyperconjugative Effect* by which the alkyl groups release electrons

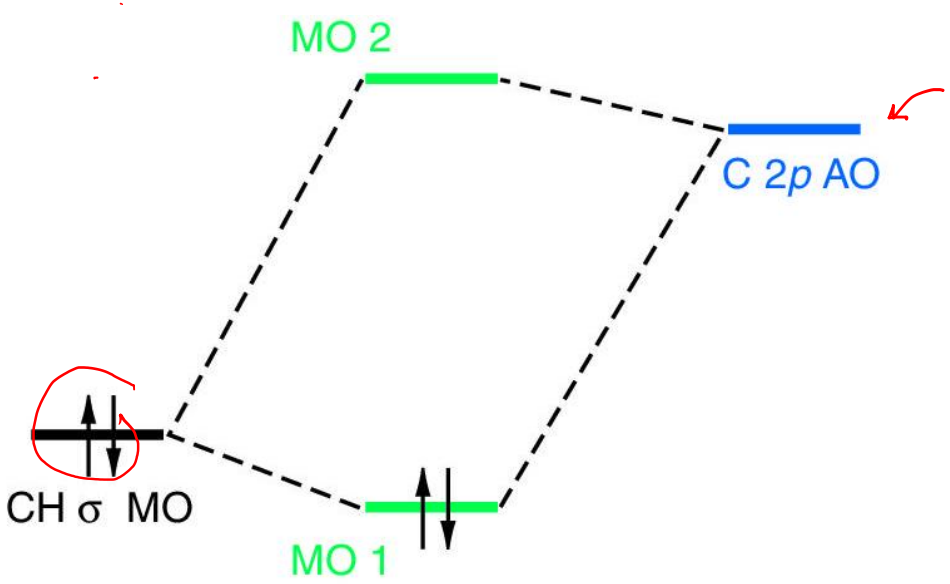


✓ *Can we understand this based on MO considerations?*

Stabilization of Tertiary Carbocations by C–H

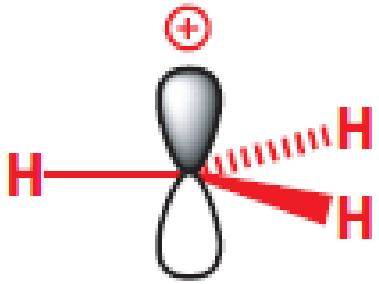
(σ-Conjugation)





- Interaction between the C-H σ-bonding MOs with the vacant 2p orbital of the carbon
- This interaction lowers the energy of *the electrons in the C-H bonding orbitals*

No σ-conjugation for CH_3^+



no stabilization: no electrons to donate into empty p orbital
note: The C–H bonds are at 90° to the empty p orbital and cannot interact with it