

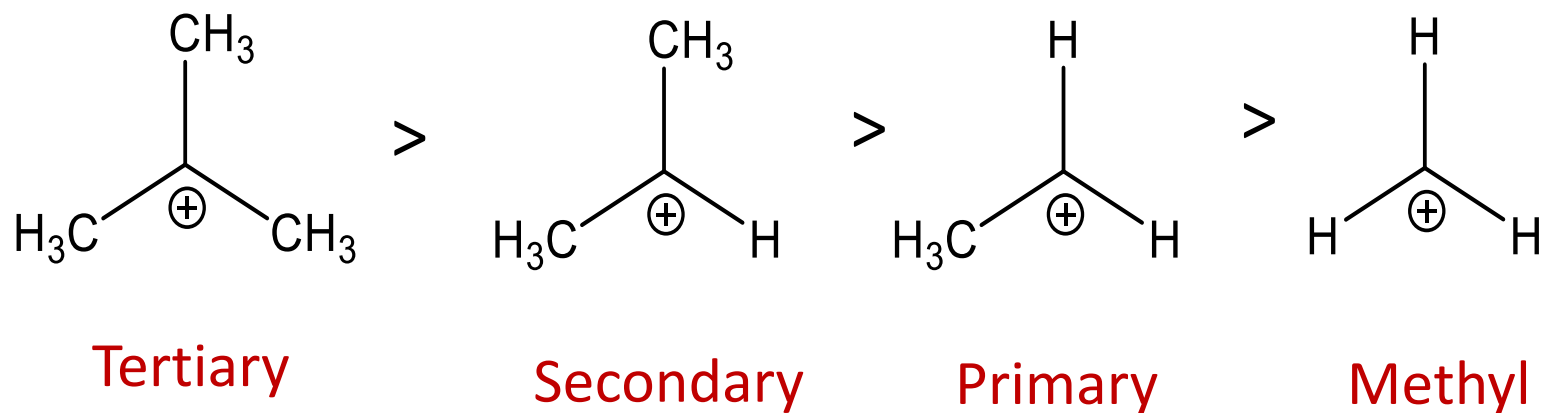
Statement: t-alkyl halides undergo much faster S_N1 reaction than methyl/primary halides

1: t-alkyl halides undergo much faster S_N1 reaction than methyl/primary halides because t-alkyl carbocations are more stable than methyl/primary carbocation

2: t-alkyl halides undergo much faster S_N1 reaction than methyl halides because the activation energy for the formation of t-alkyl carbocations is lower than methyl carbocation

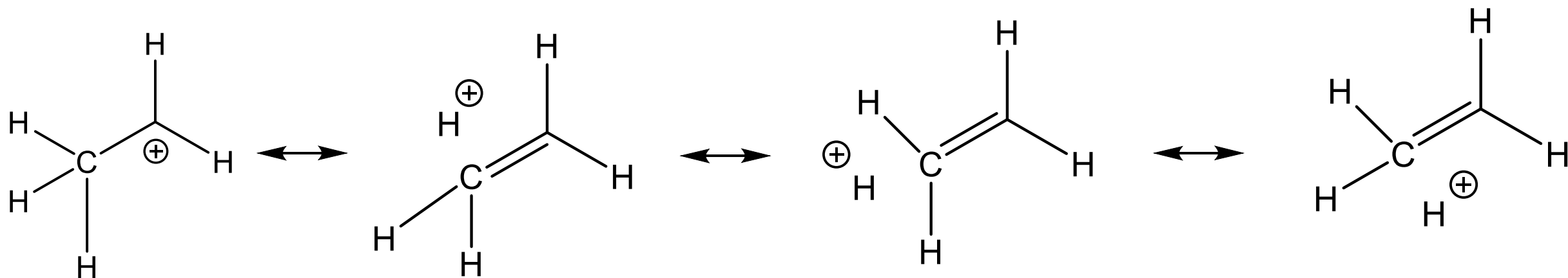
Relative Stability of Carbocations

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



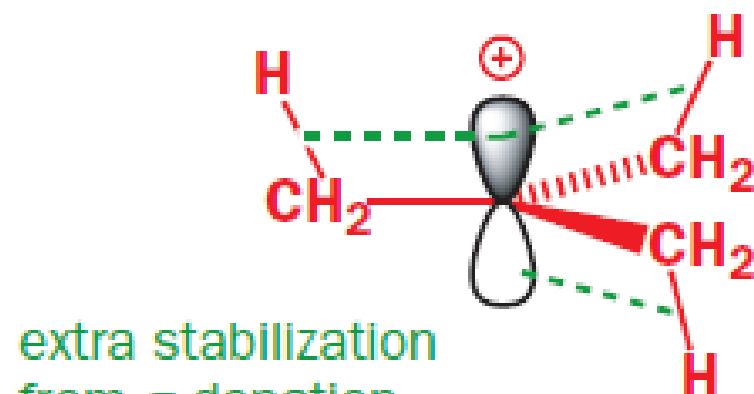
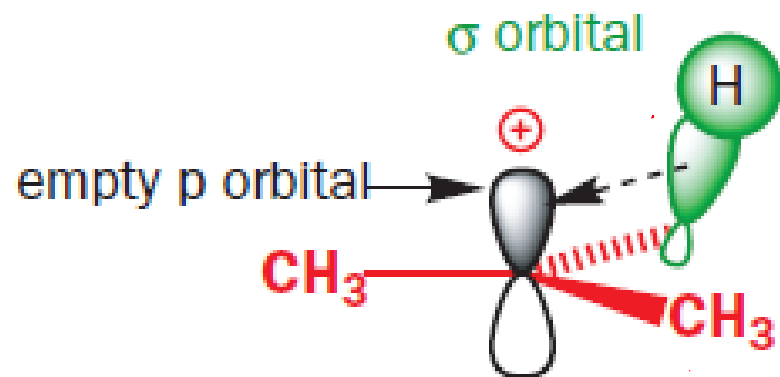
✓ This is generally explained by the +I effect of the $-\text{CH}_3$ groups

- However, there is another effect called *Hyperconjugative Effect* (VBT) by which the alkyl groups release electrons

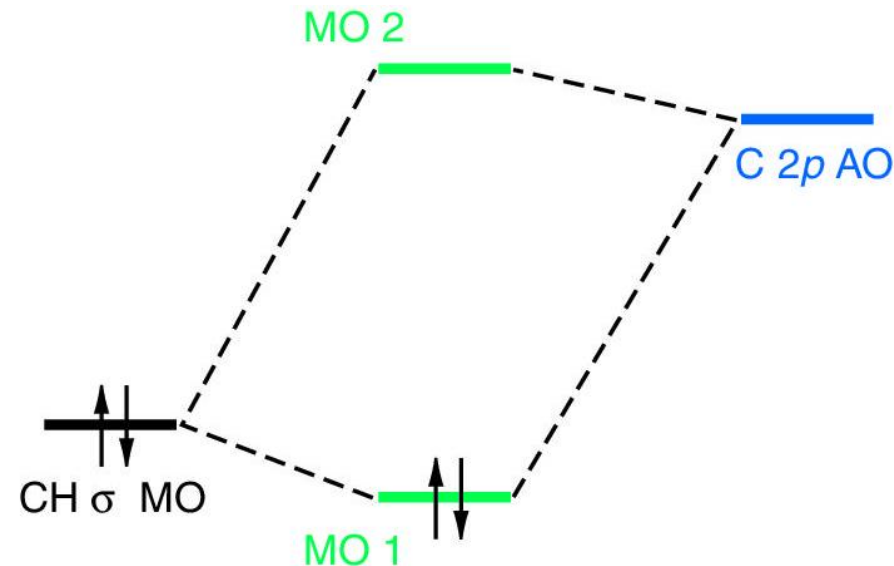


✓ *Can we understand this based on MO considerations?*

Stabilization of Tertiary Carbocations by C–H (σ -Conjugation)

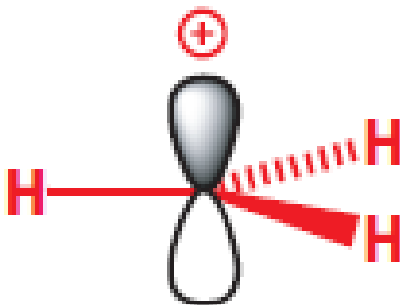


extra stabilization
from σ donation
into empty p orbital
of planar carbocation



- 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*

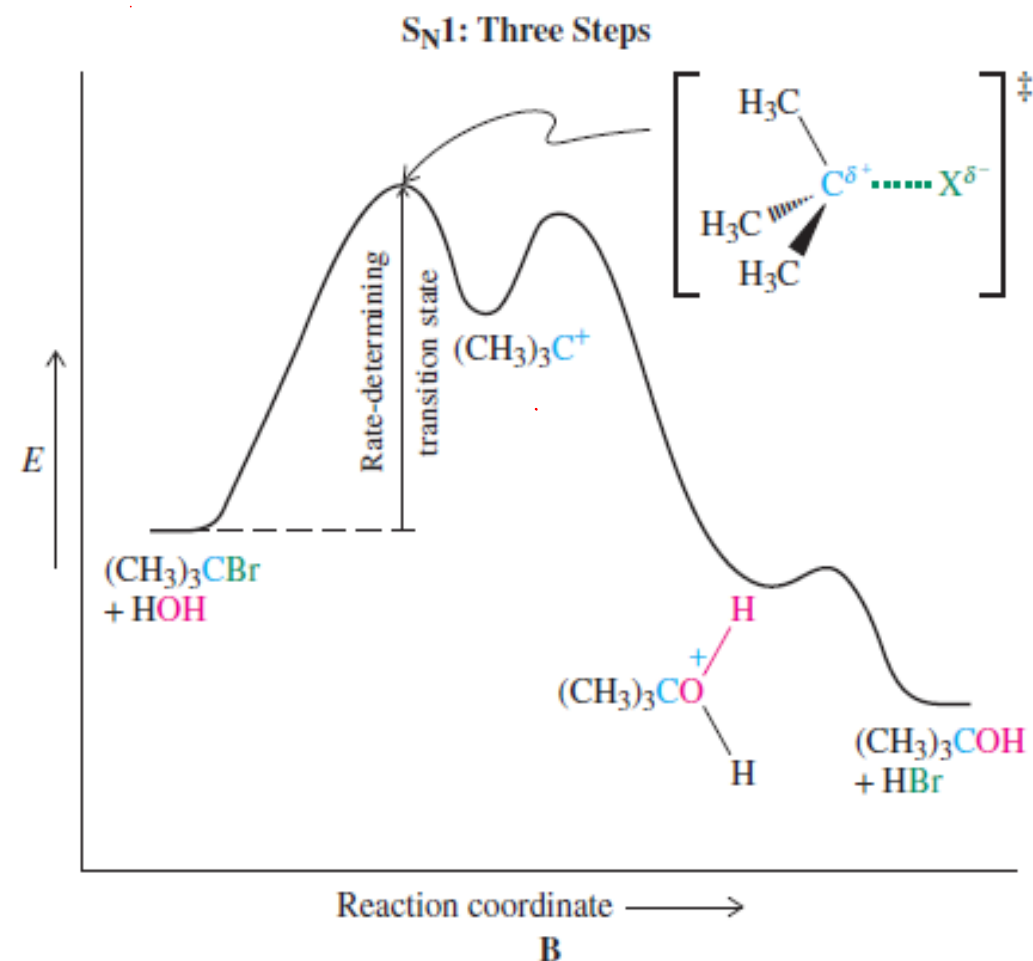
No σ -conjugation for CH_3^+



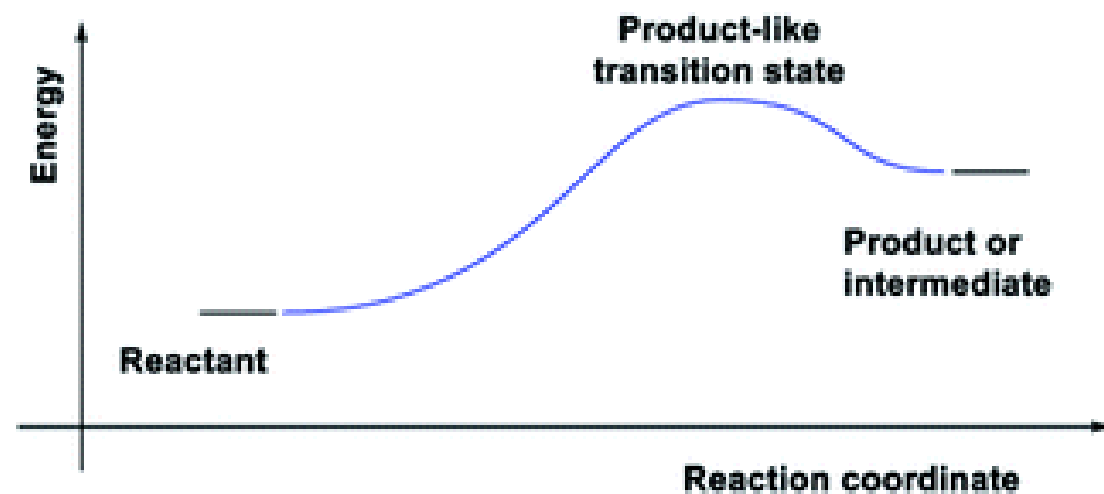
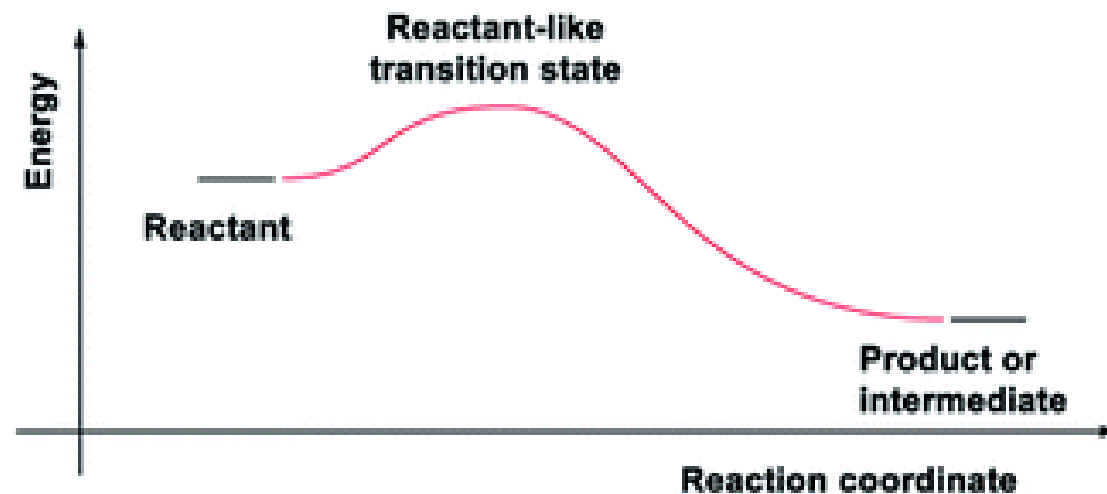
no stabilization: no electrons
to donate into empty p orbital
note: The C-H bonds are at
 90° to the empty p orbital
and cannot interact with it

- ✓ It is true that a t-butyl carbocation is more stable than methyl or primary carbocations
- ✓ However, the rate of a $\text{S}_{\text{N}}1$ reaction is dependent on the activation energy of the formation of carbocation, not on their stability

- ✓ **Fact 1:** The activation energy of the formation (E_a) of a t-alkyl carbocation is smaller than methyl/primary: *Important for S_N1 reactions*
- ✓ **Fact 2:** t-alkyl halides undergo much faster S_N1 reaction than methyl/primary halides because the activation energy for the formation of t-alkyl carbocation is lower than methyl/primary carbocation



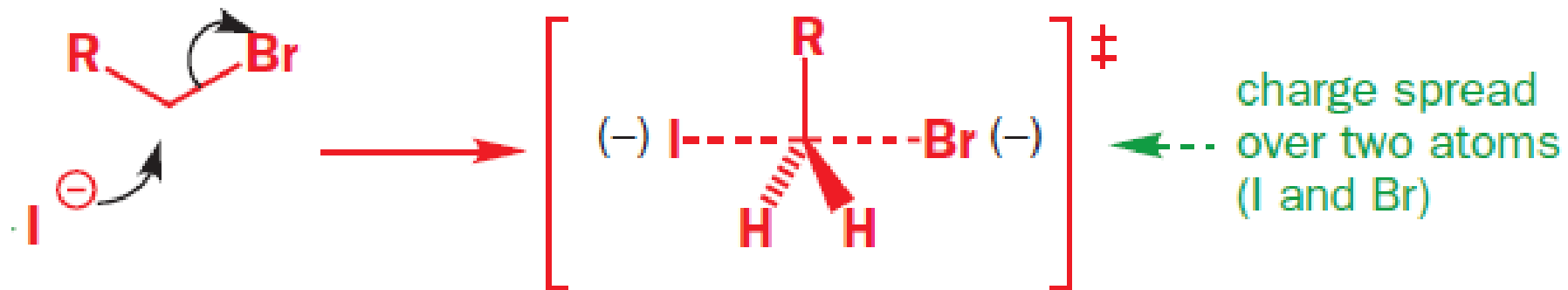
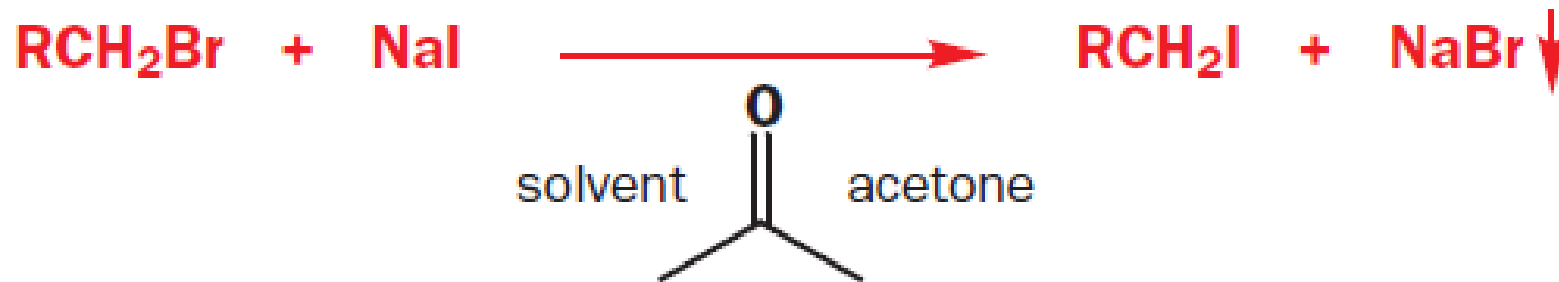
Hammond Postulate: Correlation between transition state with reactant or product structure



Solvent Effects in S_N Reactions

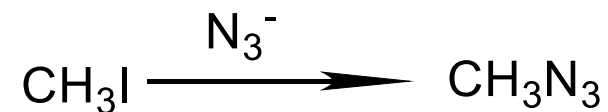
Solvent Effect: S_N2

- ✓ Typical choices: a less polar solvent for the S_N2 reaction (just polar enough to dissolve the ionic reagents)



- ✓ The most common S_N2 reactions use an anion as the nucleophile and the transition state is less polar than the localized anion as the charge is spread between two atoms
- ✓ A polar solvent solvates the anionic nucleophile and slows the reaction down
- ✓ A nonpolar solvent destabilizes the starting materials more than it destabilizes the transition state and speeds up the reaction

The following table presents rate data for the reactions of CH_3I with azide ion:



Solvent	Relative Rate	Dielectric Constant
Methanol	1	33
DMF	4.5×10^4	37

✓ The dielectric constant (ϵ) of a solvent is a measure of its polarity