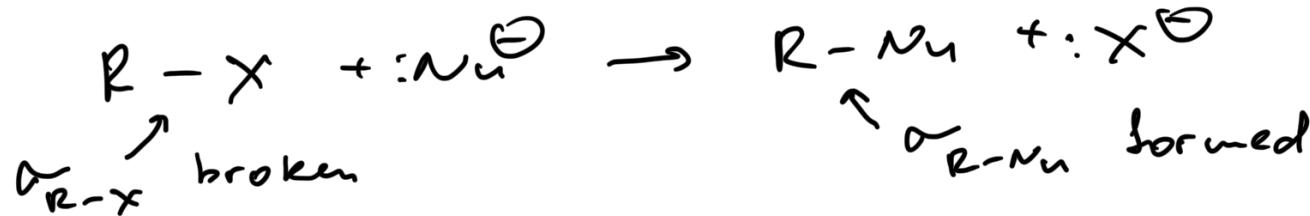
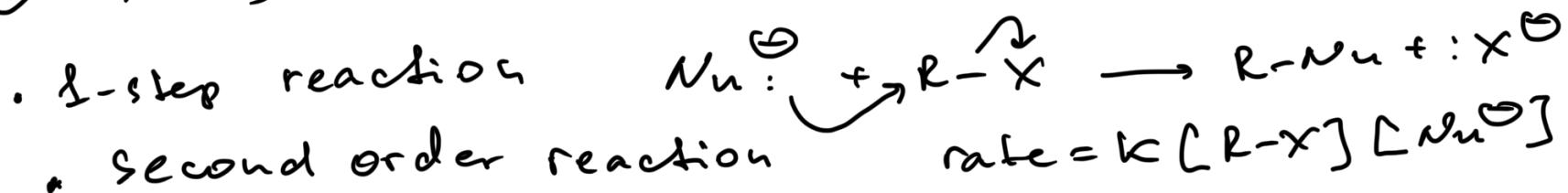


# Nucleophilic substitution: mechanisms

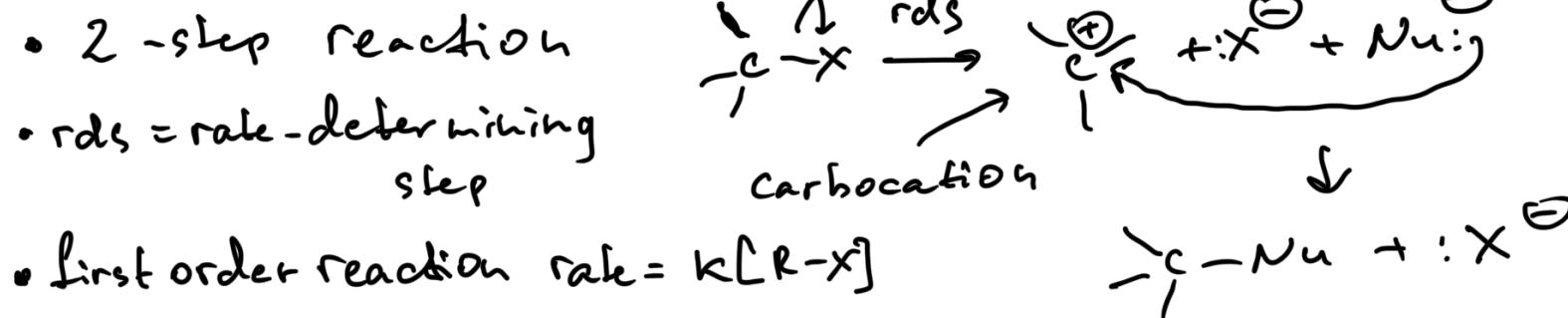
One step or two steps?



① bonds broken / formed simultaneously

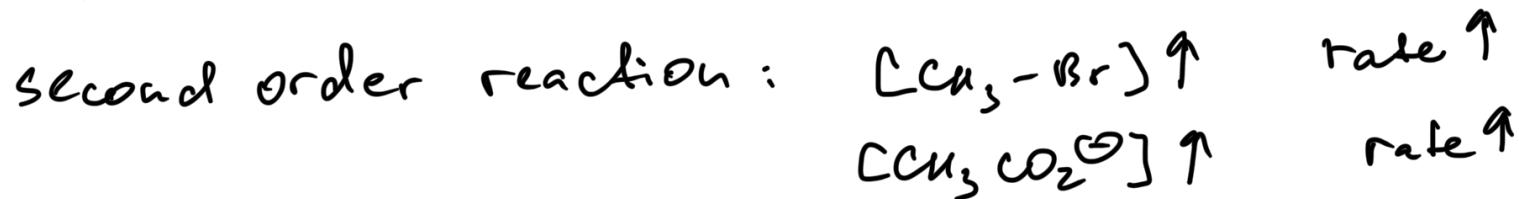


② bonds broken / formed consecutively

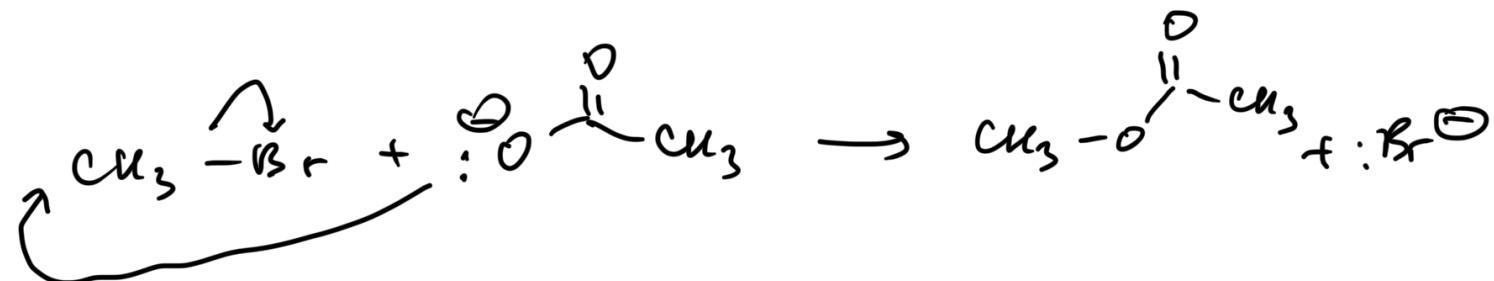


# Nucleophilic substitution: the S<sub>N</sub>2 mechanism

Substitution nucleophilic bimolecular, kinetics and mechanism



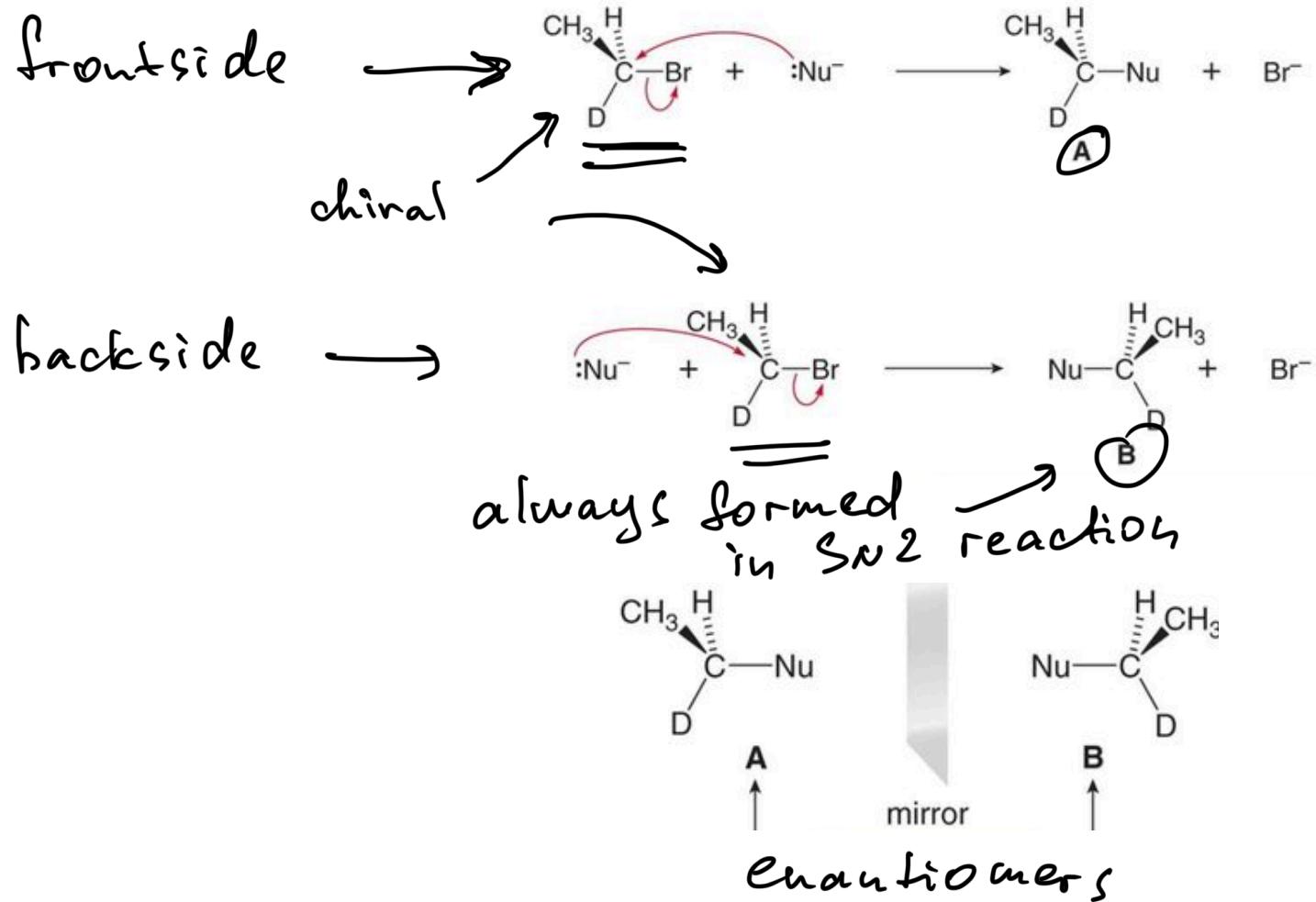
$$\text{rate} = k [\text{CH}_3\text{-Br}][\text{Cu}_3\text{CO}_2^-]$$



- S<sub>N</sub>2 reaction

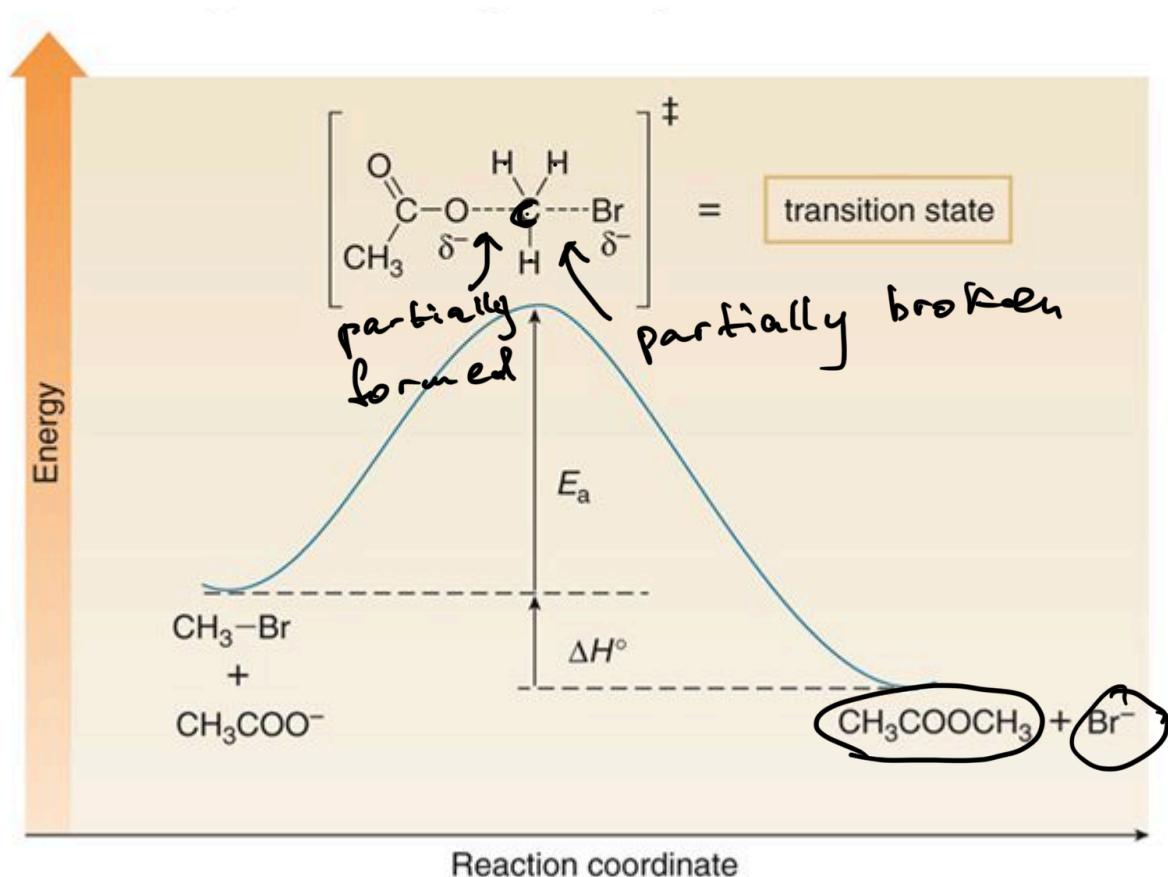
# Nucleophilic substitution: the S<sub>N</sub>2 mechanism

Frontside or backside? Stereochemistry of the S<sub>N</sub>2 reaction, Walden inversion



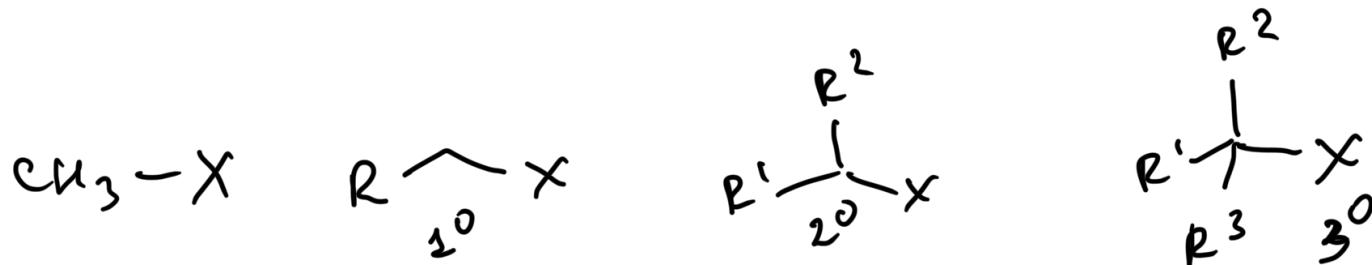
# Nucleophilic substitution: the S<sub>N</sub>2 mechanism

Substitution nucleophilic bimolecular, mechanism and energy diagram



# Nucleophilic substitution: the S<sub>N</sub>2 mechanism

Effect of the R group (1°, 2°, 3°) on the S<sub>N</sub>2 reaction

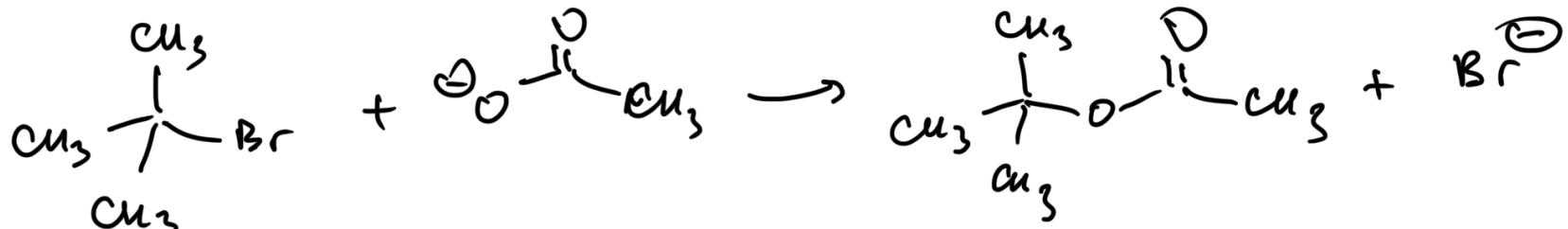


←  
rate of S<sub>N</sub>2 reaction  
increases  
←  
steric hindrance  
decreases

- CH<sub>3</sub>- and 1° undergo fast S<sub>N</sub>2
- 2° undergo S<sub>N</sub>2 slowly
- 3° do not undergo S<sub>N</sub>2

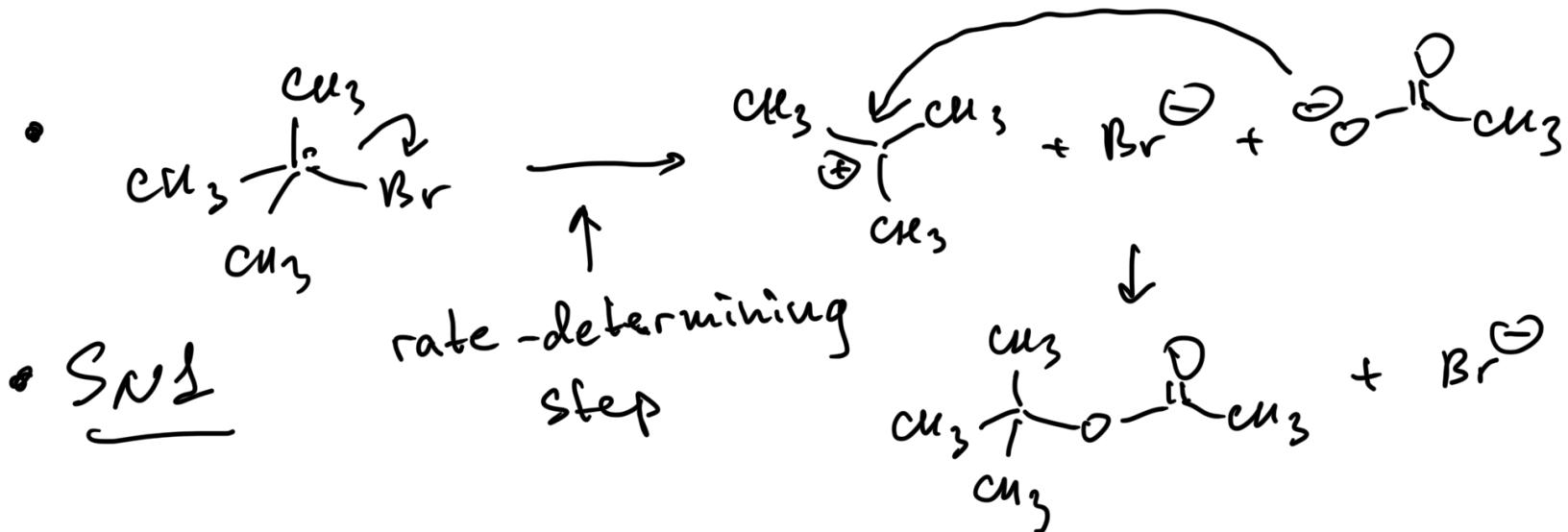
# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

Substitution nucleophilic unimolecular, kinetics and mechanism



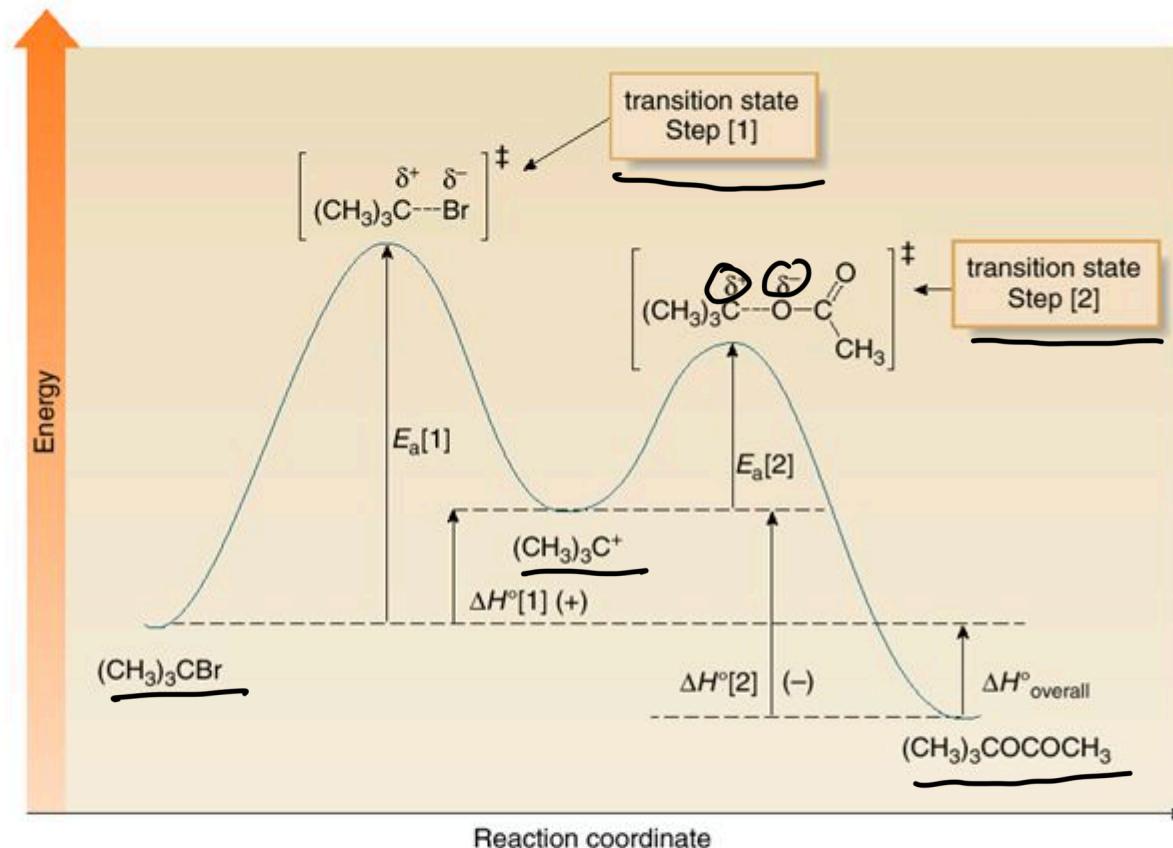
$$\text{rate} = k[t\text{-BuBr}]$$

- first order reaction



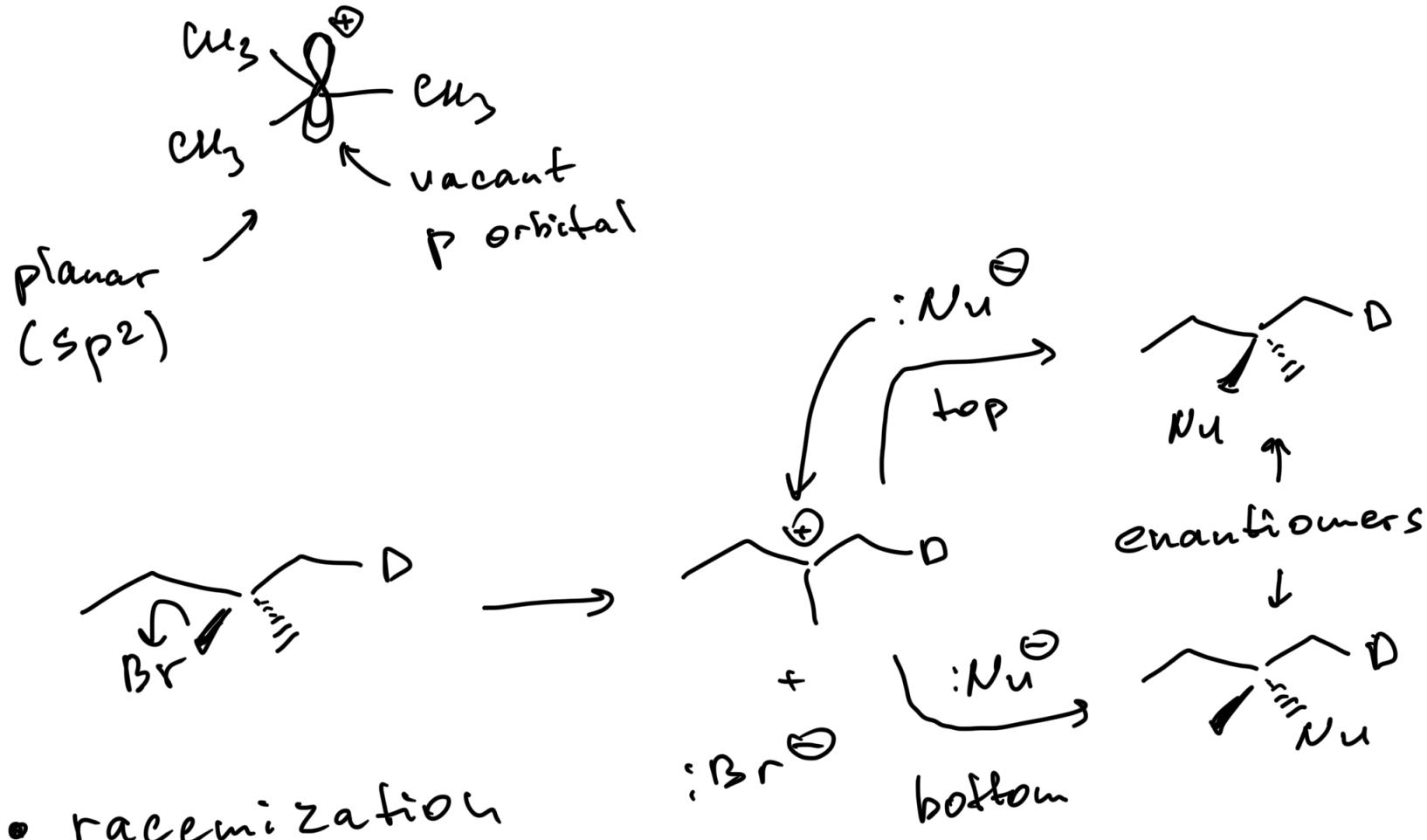
# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

Substitution nucleophilic unimolecular, energy diagram



# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

Stereochemistry of the S<sub>N</sub>1 reaction, racemization

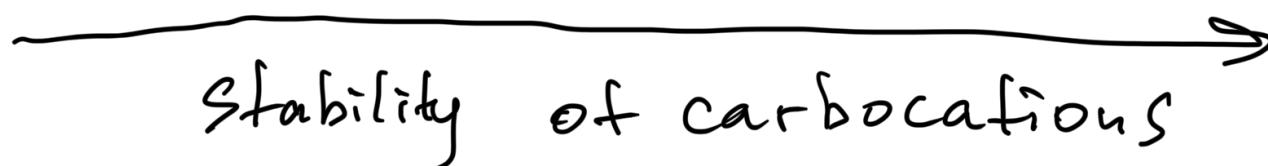
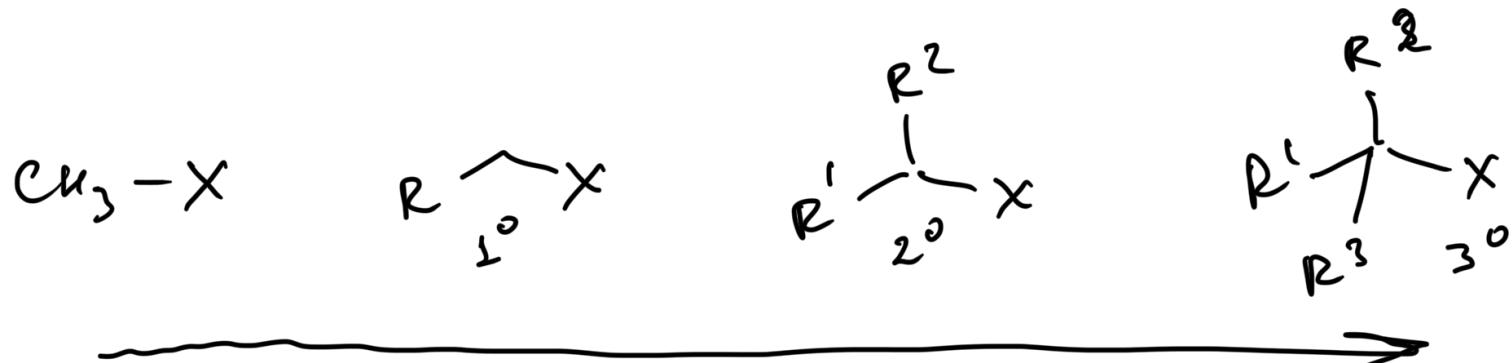


- racemization

(stereoschemical information is lost)

# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

Effect of the R group (1°, 2°, 3°) on the S<sub>N</sub>1 reaction

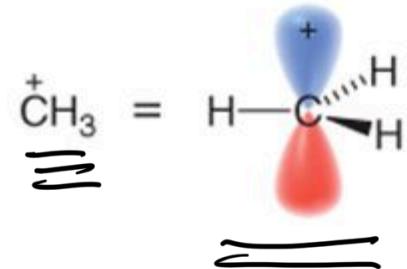


- 3° alkyl halides undergo fast S<sub>N</sub>1
- 2° undergo slow S<sub>N</sub>1
  - CH<sub>3</sub>- and 1° do not react

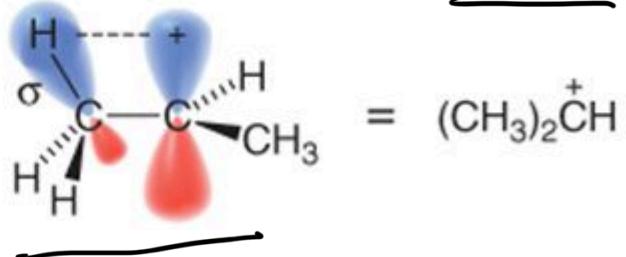
# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

Carbocation stability, hyperconjugation

$\text{p}$  orbital orthogonal  
to  $\sigma_{\text{C-H}}$



$\sigma_{\text{C-H}}$  donates electron density to vacant  $\text{p}$  orbital



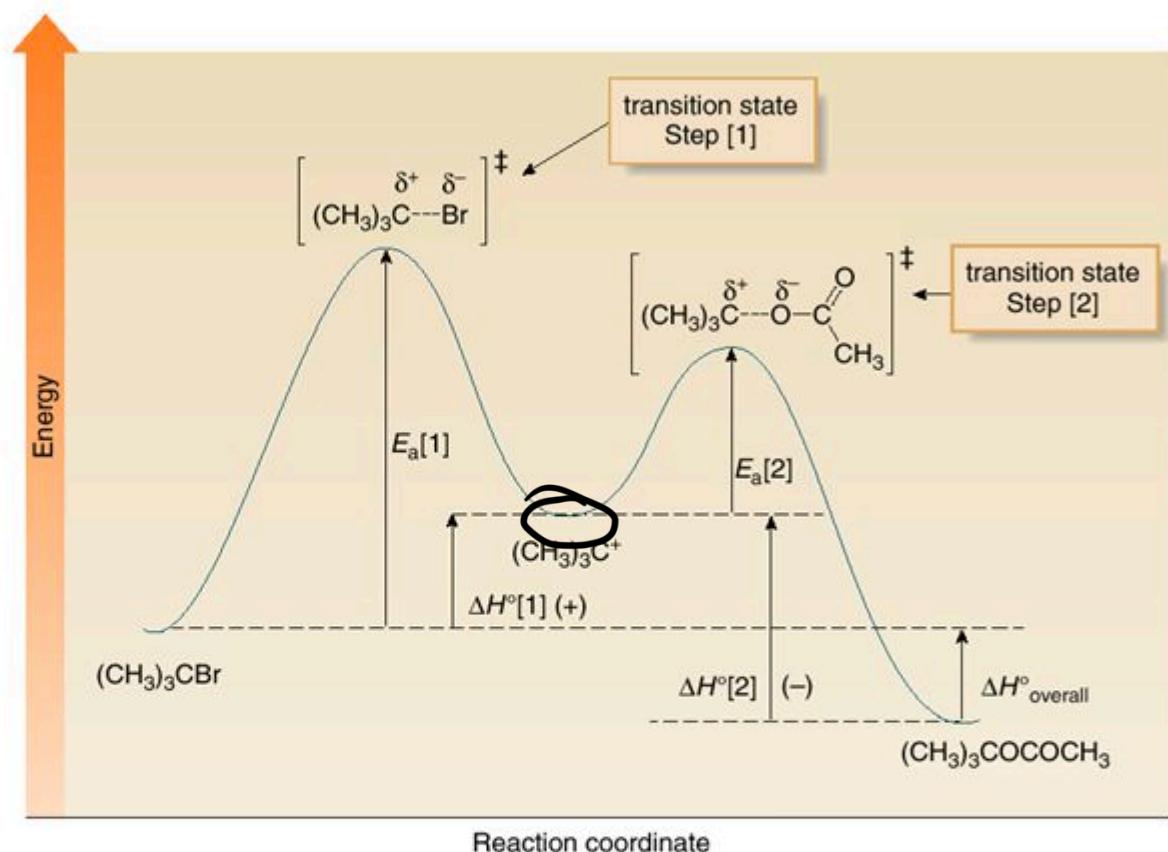
hyperconjugation

- more substituents  $\rightarrow$  more hyperconjugation

# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

Stability of carbocations and the S<sub>N</sub>1 reaction

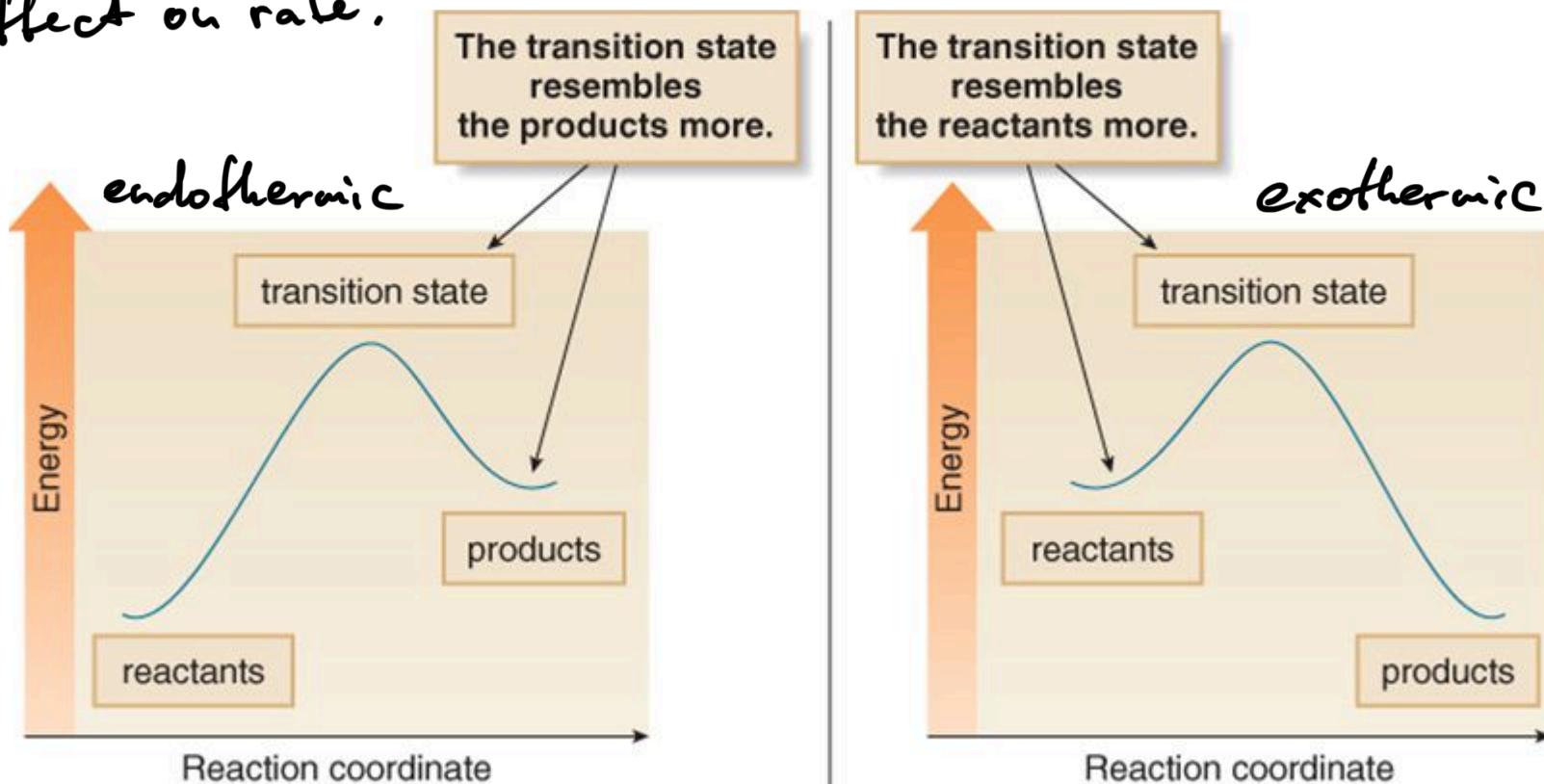
↖ how does it affect the rate of S<sub>N</sub>1?



# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

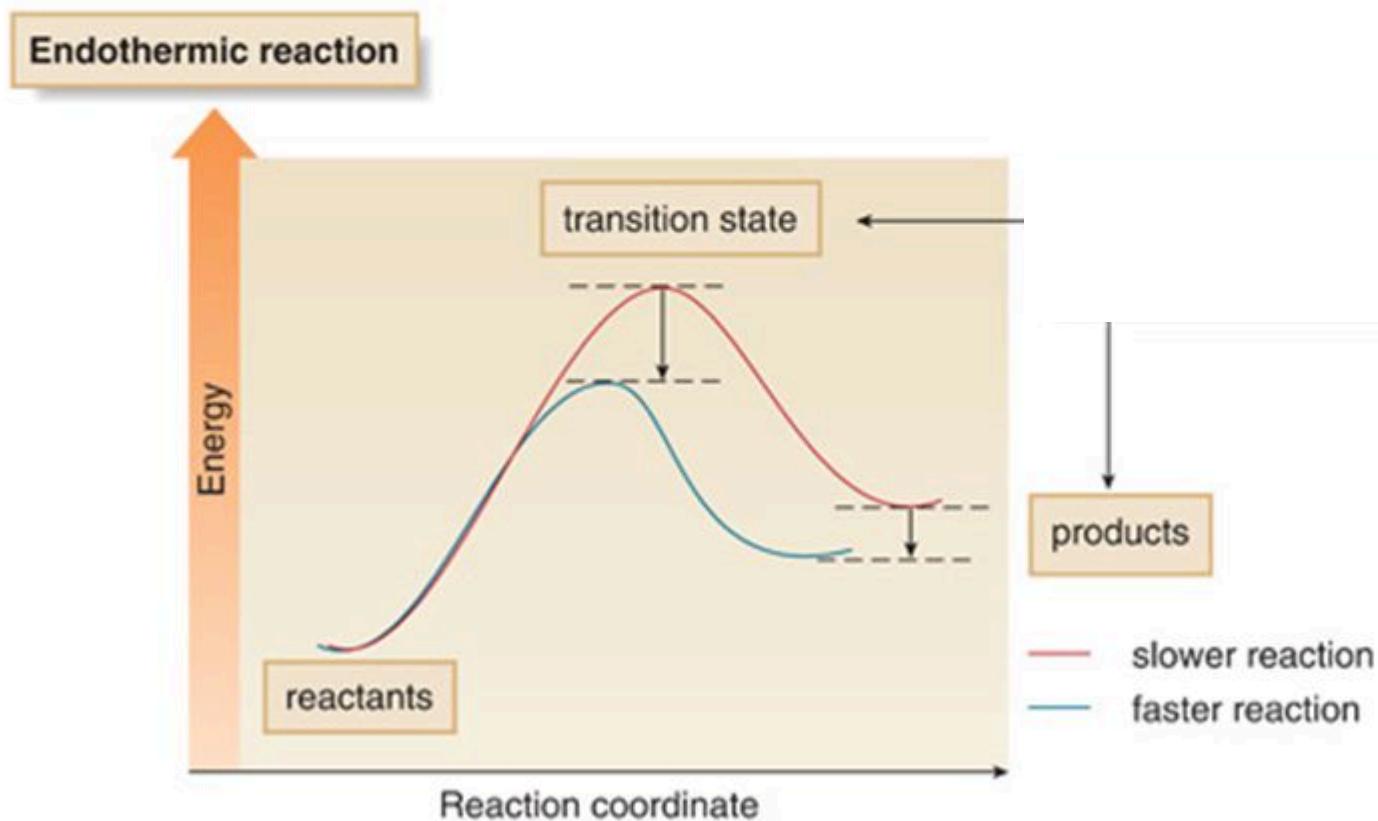
The Hammond postulate : relates energy of Transition State and relative energies of starting materials and products

effect on rate!



# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

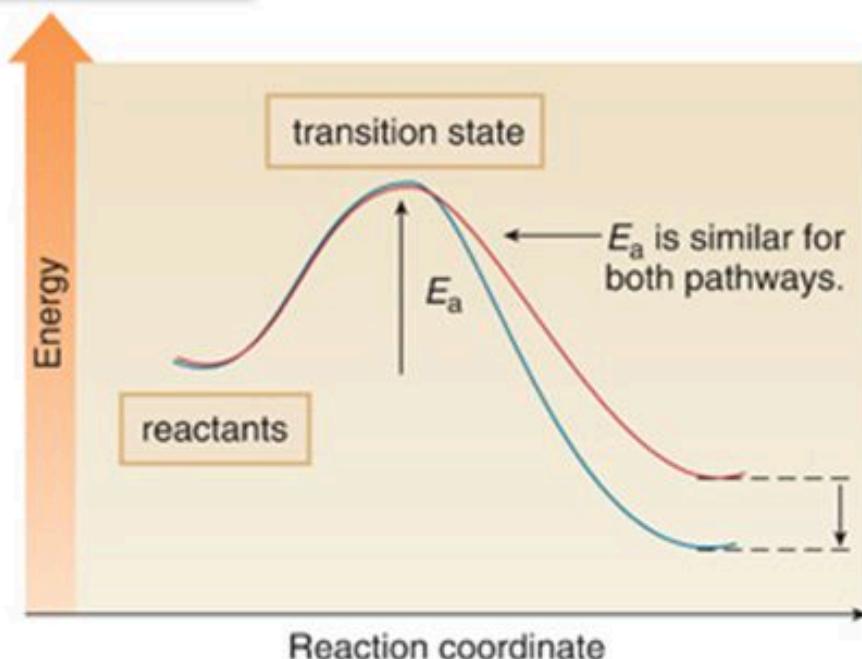
The Hammond postulate



# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

The Hammond postulate

Exothermic reaction

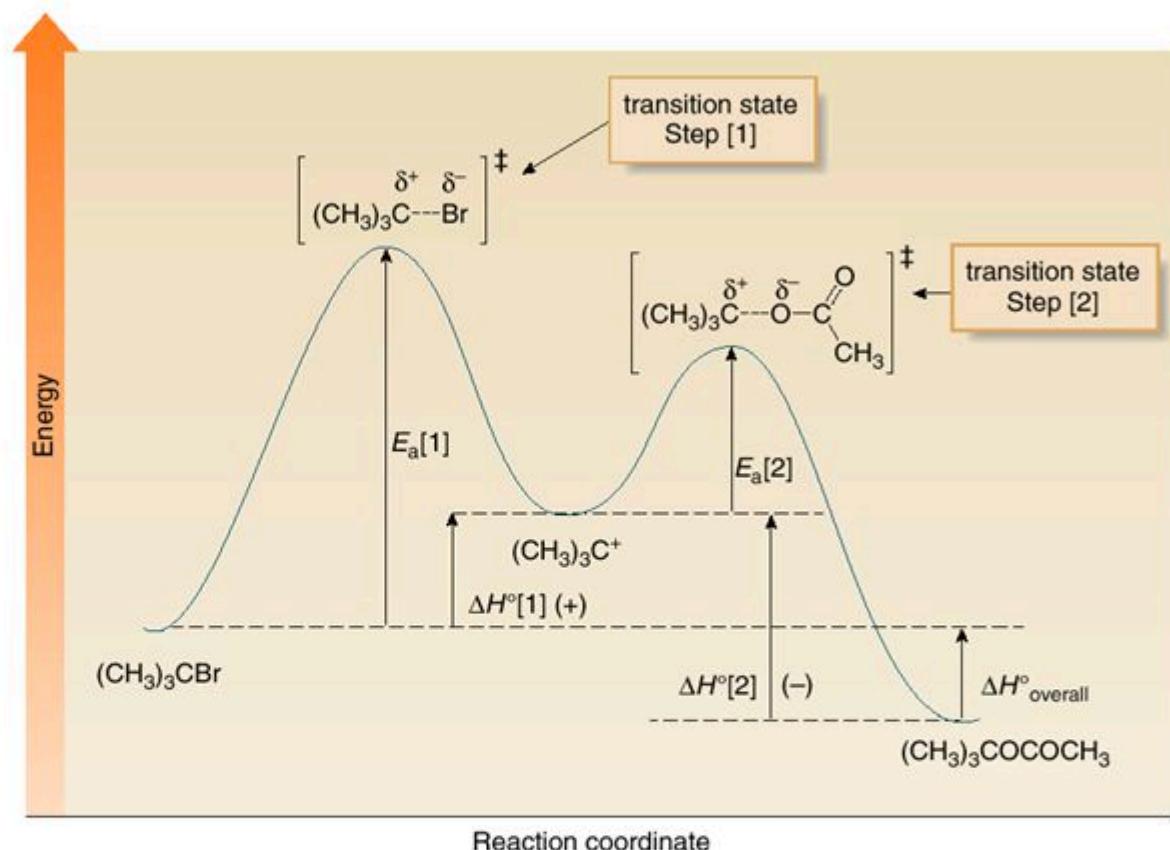


Decreasing the energy of the product has little effect on the energy of the transition state.

products

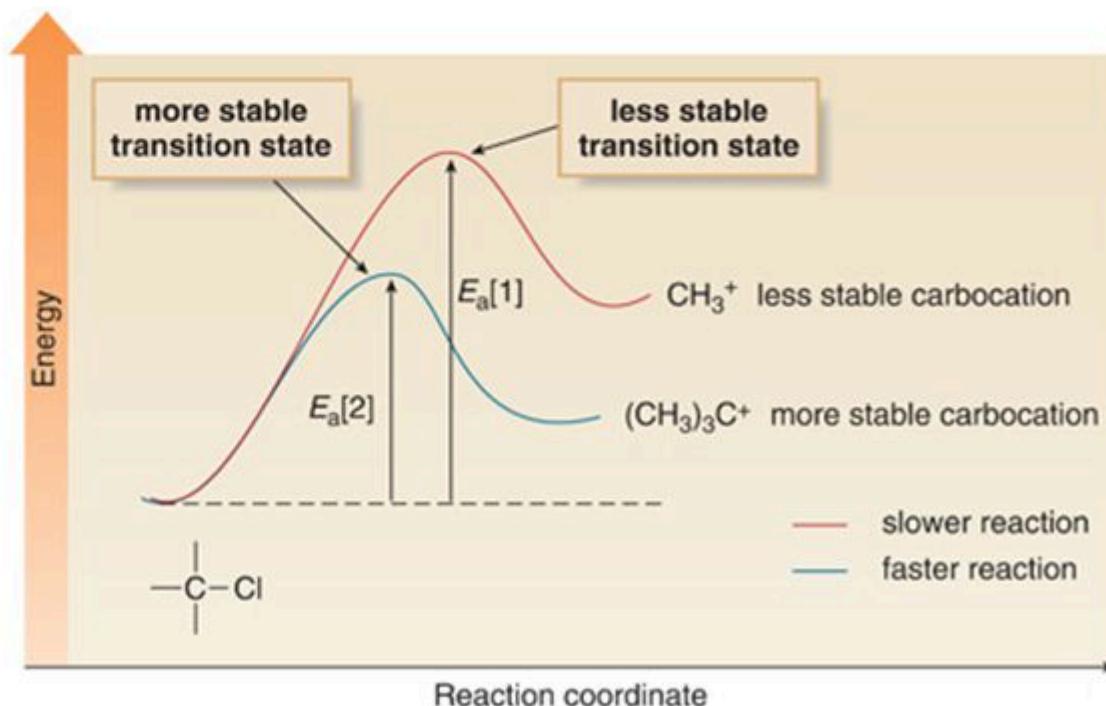
# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

The Hammond postulate and the S<sub>N</sub>1 reaction



# Nucleophilic substitution: the S<sub>N</sub>1 mechanism

The Hammond postulate and the S<sub>N</sub>1 reaction



# **Nucleophilic substitution: S<sub>N</sub>2 or S<sub>N</sub>1 mechanism?**

Factors governing the mechanism of the substitution reaction

# **Nucleophilic substitution: S<sub>N</sub>2 or S<sub>N</sub>1 mechanism?**

Effect of the alkyl group

# **Nucleophilic substitution: S<sub>N</sub>2 or S<sub>N</sub>1 mechanism?**

Effect of the nucleophile

# **Nucleophilic substitution: S<sub>N</sub>2 or S<sub>N</sub>1 mechanism?**

Effect of the leaving group

# **Nucleophilic substitution: S<sub>N</sub>2 or S<sub>N</sub>1 mechanism?**

Effect of the solvent