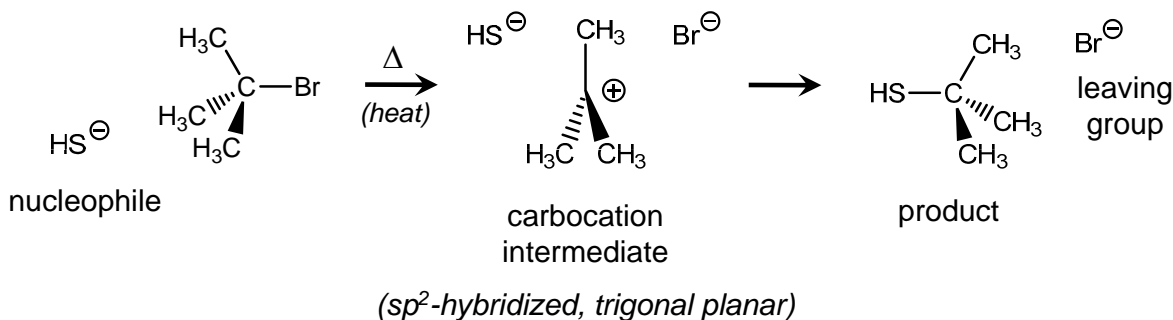


1st Order Nucleophilic Substitution (S_N1)

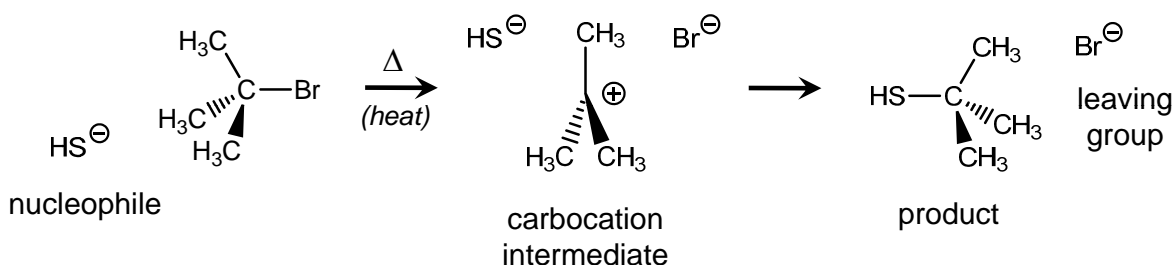
Like S_N2, S_N1 is another reaction mechanism that substitutes one functional group for another.



The outcomes of S_N2 and S_N1 reactions are the same. So,

- What are the differences between the two mechanisms?
- How do we know which mechanism is preferred?

Features of S_N1

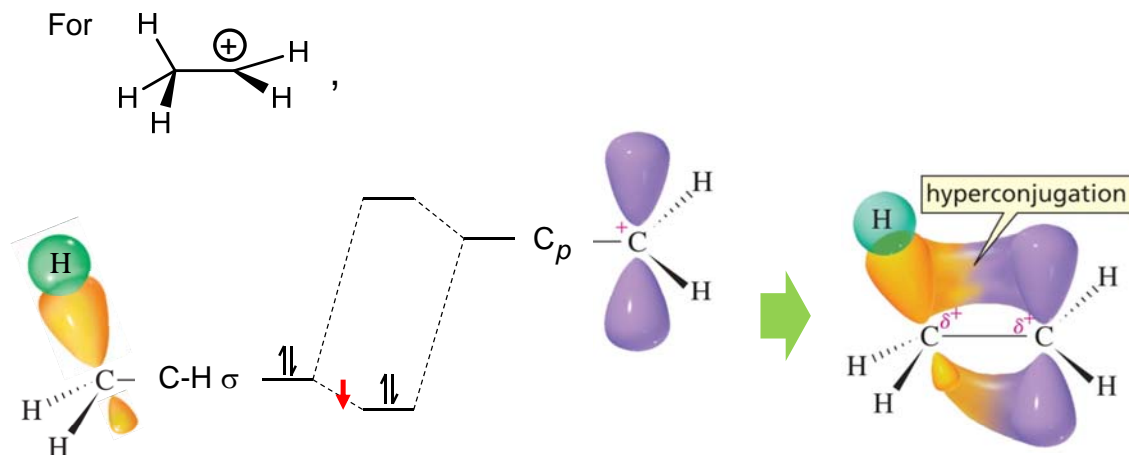


1st Order because only electrophile involved in rate expression:

$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

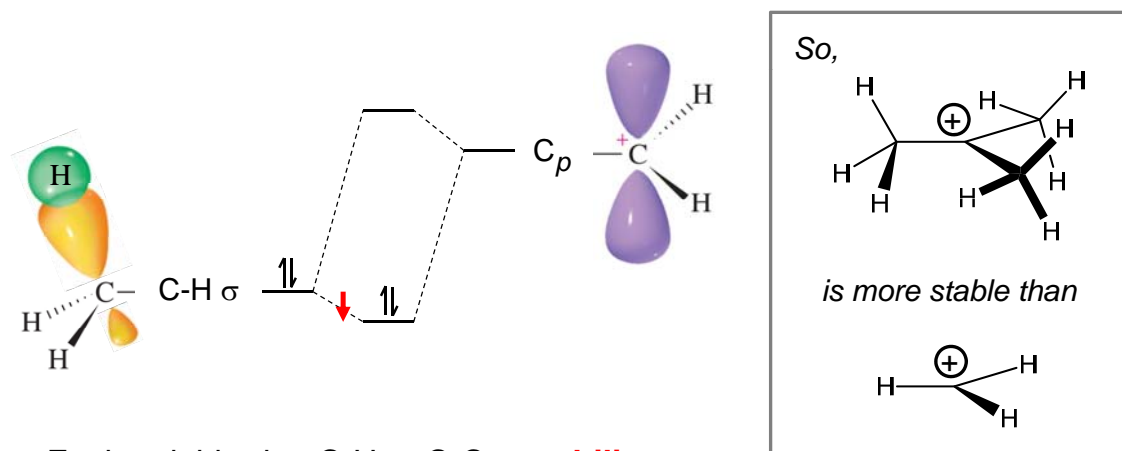
- In S_N2, departure of leaving group and arrival of nucleophile are **concerted**.
- In S_N1, mechanism is **stepwise**. Leaving group departs to form discrete intermediate, then nucleophile adds.

Carbocations Are Stabilized by Hyperconjugation



Each neighboring C-H σ **stabilizes** the empty C_p orbital in a carbocation. (C-C σ also stabilizes.)

More Substituted Carbocations Are More Stable



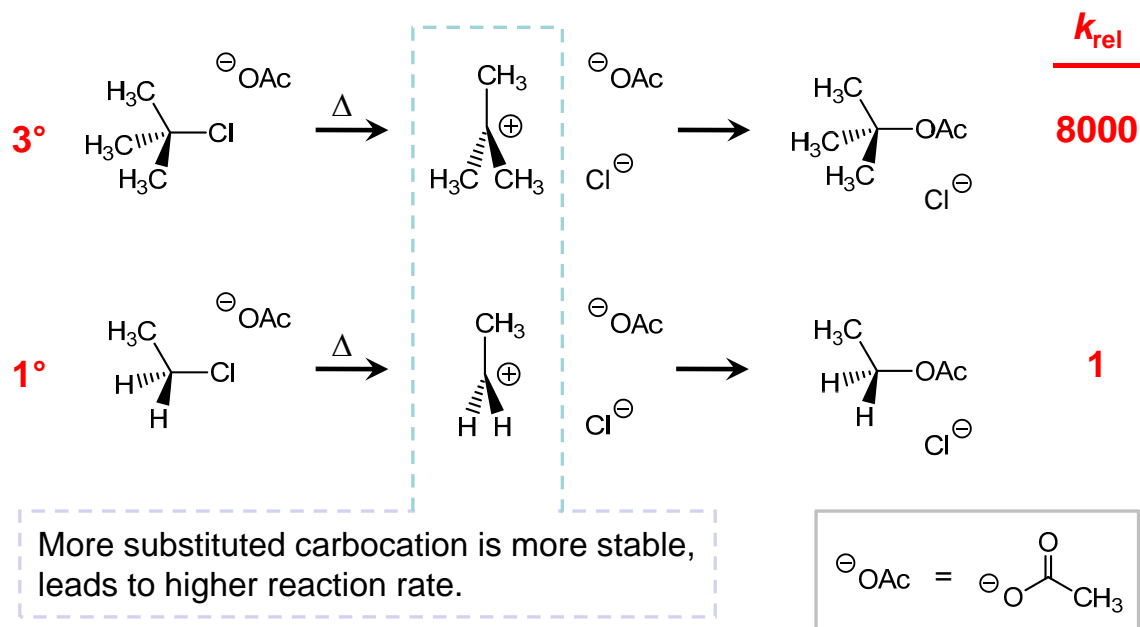
Each neighboring C-H or C-C σ **stabilizes** the empty C_p orbital in a carbocation.

So, the more C-H/C-C's there are, the more stable the cation is.

Stability trend for R_3C^+ : $3^\circ > 2^\circ > 1^\circ > CH_3$

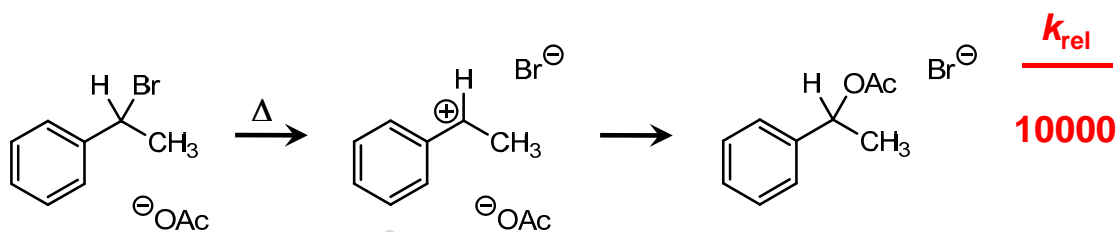
S_N1 Occurs When the Carbocation Intermediate is Most Stable

Relative rates of S_N1 reactions:



S_N1 Occurs When the Carbocation Intermediate is Most Stable

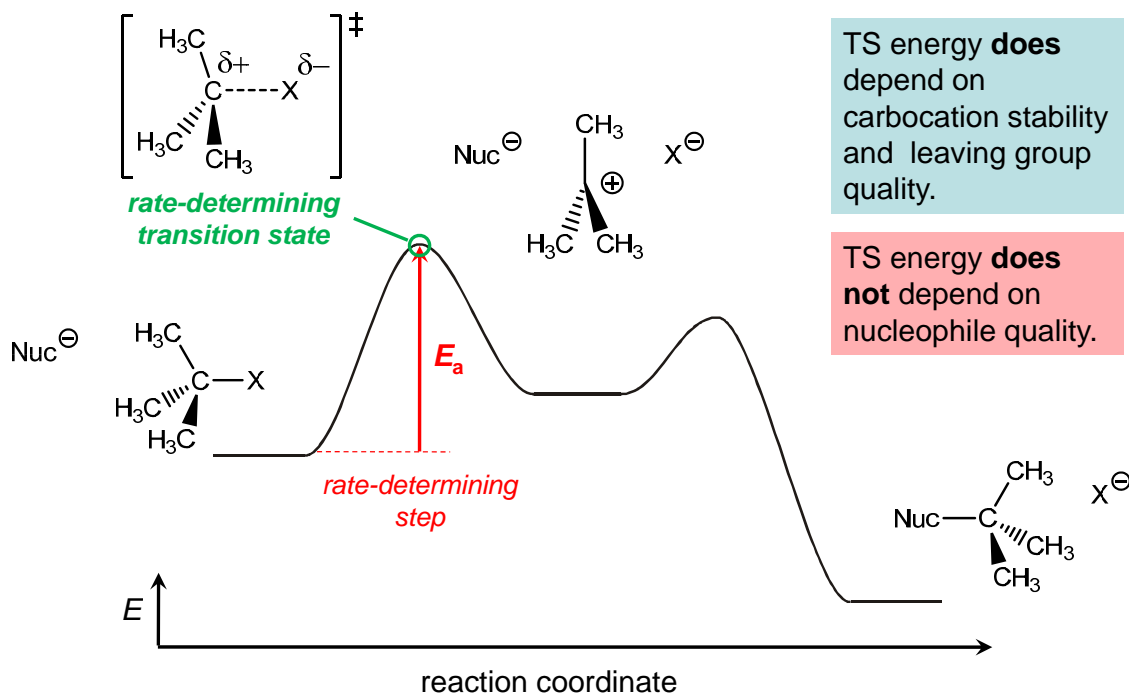
Carbocations also stabilized by resonance.



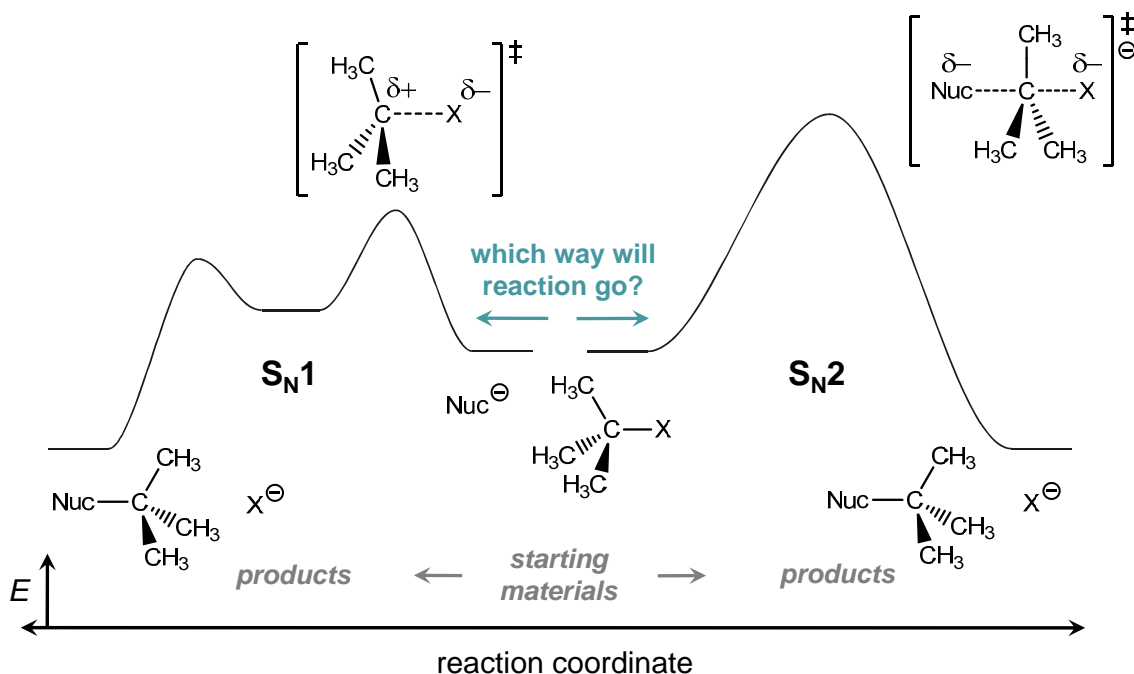
resonance structures?

Cation is stabilized by resonance, so S_N1 mechanism operates here.
Resonance is usually even more important than substitution.

Potential Energy Diagram for S_N1



Substitution Reactions Choose S_N1 or S_N2 (or Both)



Substitution Reactions Choose S_N1 or S_N2 (or Both)

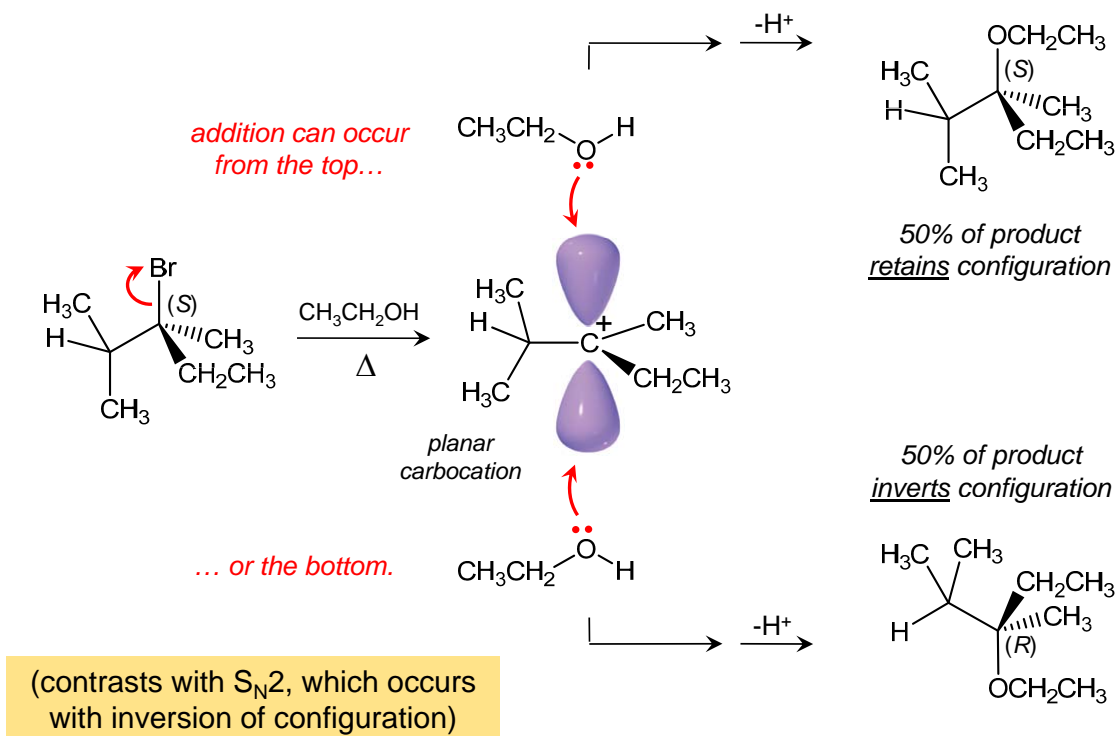
Promoting factors:

| | S_N1 | S_N2 |
|------------------|---|--------------------------------|
| nucleophile | weak nucleophile OK high concentration helps | strong nucleophile required |
| substrate | $3^\circ > 2^\circ$ | $CH_3 > 1^\circ > 2^\circ$ |
| leaving group | good leaving group required | good leaving group required |
| solvent | very polar solvent helps (H_2O , DMF, DMSO, CH_3CN) | polar, but not too polar |

Proposing Multistep Reaction Mechanisms ("Electron Pushing")

- Focus on getting from starting materials to products.
- Make sure each step is balanced; atoms, electrons and charge should be conserved.
- Don't draw multiple steps as one. Each step (including acid-base exchange) creates new, discrete species.
- Make sure intermediates are compatible with reaction conditions.

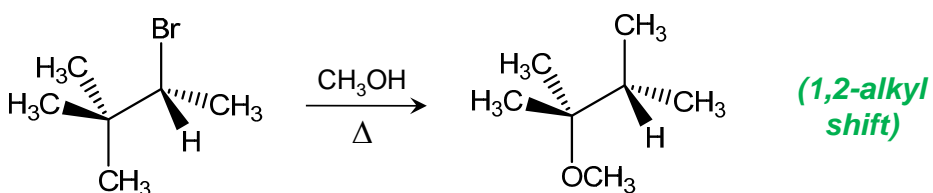
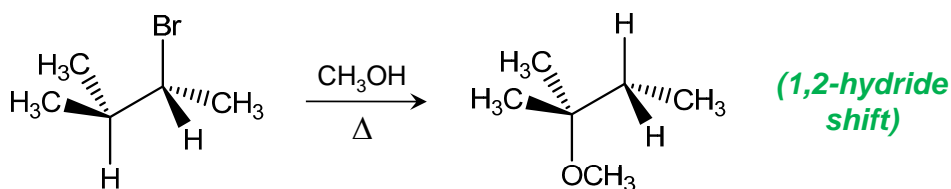
S_N1 Reactions Produce Racemates



Carbocation Rearrangements

A carbocation will rearrange (by hydride or alkyl shift) if it can form a more stable carbocation.

Explains:



S_N1 and S_N2 Occur at sp^3 -Hybridized Carbons Only

