S_{N1} Mechanism

UCI Chem 51A
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Goals

After this lesson you should be able to:

- Identify and draw an $S_N 1$ mechanism
- Describe the experimental evidence that supports the $S_N 1$ mechanism
- Identify electrophiles that are likely to undergo an $S_N 1$ mechanism
- Rank and explain relative stabilities of carbocation intermediates
- Explain the importance of the leaving group in $S_N 1$ reactions
- Explain the effect of the nucleophile on $S_N 1$ reactions
- Explain the effect of the solvent on $S_N 1$ reactions
- Predict and explain the stereochemical outcome of an $S_N 1$ reaction at a stereocenter
Nucleophilic Substitution Mechanisms

All at once:

\[ \text{C-X} + \text{Nu}^- \rightarrow \text{C-Nu} + \text{X}^- \]

Break, then form:

\[ \text{C-X} \rightarrow \text{C}^+ + \text{X}^- \xrightarrow{\text{Nu}} \text{C-Nu} \]
The S_N 1 Mechanism

C-X → C^+ + X^- → C-Nu
How Do We Know?

Rates
rate = k [EI]
Rate law derived experimentally.
Only electrophile both involved in RDS.

Intermediates
Carbocation intermediates identified experimentally.

Stereochemistry
Effects on stereocenters support $S_{N1}$
The Leaving Group

* All nucleophilic substitution reactions require a good leaving group.

Better LG = lower energy

Increases amount that intermediate formation favored
The Electrophilic Carbon

Type of C matters

\[ 3^\circ > 2^\circ > 1^\circ > \text{methyl} \]

Why? Carbocation stability!

No RXN!
Carbocation Stability

$3^\circ > 2^\circ > 1^\circ > \text{methyl}$

**Hyperconjugation**

Neighboring $\sigma_{\text{C-H}}$ bonds can donate small amount of $e^-$ density. More neighboring bonds = more donation = lower energy.
The Hammond Postulate

- TS^+ resembles structure that is closest to it in energy
- For an endothermic process, TS^+ is more similar to product than reactant
- Anything that lowers energy of product also lowers energy of TS^+

![Reaction Coordinate Graph]
Applying Hammond Postulate to $S_{N1}$ Mechanism

* Whatever stabilizes carbocation stabilizes $TS^t$
* Stabilizes $TS^t = \text{lower } E_a = \text{faster rxn!}$

So...

$3^o > 2^o > 1^o > \text{methyl}$

Other ways to stabilize carbocation?
Benzyl and Allyl Carbocations

* Resonance!
Carbocation Summary

- Stabilized by hyperconjugation
- 1° & methyl too high energy to form
- Stabilized by resonance
- Can be stabilized by both simultaneously! Even better!
The Nucleophile

* $S_{N1}$ reactions are favored by **weak** nucleophiles

$S_{N1}$ reactions in competition with $S_{N2}$ reactions

Strong Nu means faster rate for $S_{N2}$
No time for $S_{N1}$!

Common $S_{N1}$ Nu
The Solvent

* $S_{N1}$ reactions are favored by **POLAR PROTIC** solvents

$H_2O$  $EtOH$  $MeOH$

Why?
Stereochemistry and
The $S_{N1}$ Mechanism

* Carbocations = trigonal planar
S\textsubscript{N}1 at Stereocenter Example
**S\textsubscript{N}1 Summary**

* Rate = 1st order
* Mechanism = 2 steps
* Electrophile: benzyl, ally, 3° > 2°...
  * no 1°, no methyl
* LG = good LG required
* Nu = weak Nu favors S\textsubscript{N}1
* Solvent = polar protic solvent favors S\textsubscript{N}1
* Stereochemistry = racemization of stereocenter

University of Surrey summary video
http://www.youtube.com/watch?v=JmcVgE2WKBE
Wrapping Up

* Practice drawing mechanisms for $S_{N1}$ reactions
* Practice predicting which electrophiles are most likely to undergo $S_{N1}$ reactions
* Practice comparing carbocation stabilities
* Practice drawing the products for an $S_{N1}$ reaction at a stereocenter