Last Time

\[ S_N^2 \text{ Reaction} \]

\[ \text{HO}^- + C-\text{Cl} \xrightarrow{H^+} \text{HO}^\cdot C^\cdot H + \text{Cl}^- \]

*concerted reaction

\[ \Rightarrow \text{Bimolecular Kinetics: Rate} = K [\text{OH}][\text{CH}_3\text{Cl}] \]

\[ \Rightarrow \text{Inversion of config. @ carbon} \]

\[ \Rightarrow \text{Pentacoordinate T.S.} = : \text{Nucleophile attacked} \sigma^* \text{orb. otherwise can't make} \]

\[ \begin{bmatrix} \text{S}^- & \text{H}^- \text{C}^- & \text{S}^- \\ \text{H}^- \text{C}^- & \text{S}^- \end{bmatrix} \]

\[ \Rightarrow \text{this species has no inherent lifetime} \]

Today

\[ S_N^1 \text{ Reaction} \]

\[ \text{CH}_3^- \text{C}^- \text{Cl} + \text{tBuOH} \rightarrow (\text{CH}_3)_3\text{C}^-\text{OH} + \text{Cl}^- \]

Electrophile \quad \text{nucleophile}

\[ \Rightarrow \text{Rate} = K [\text{tBuCl}] \quad \times \text{no} [\text{OH}] \text{ dependence} \]
Mechanism: Step-wise!

1. Ionization of C-Cl bond

\[ \text{C-Cl} \rightarrow \text{Cl}^- + \text{Cl}^+ \]

(A) (see Ta sym. on C!)

2. Pretend this is in water (can be others, too)

\[ \text{R-Cl} + \text{H}_2\text{O} \rightarrow \text{R-C-O-H} \]

3. Loss of proton with general base (\( \text{B} \))

\[ \text{R-C-Cl} \rightarrow \text{R-C-O-H} \]

Step 1 \( \rightarrow \) carbocation formation is rate determining step (R.D.S)!!

Energy Diagram: \( S_N^1 \)

[Diagram showing energy profile with carbocation as intermediate and steps labeled SM, Prop, Hal, and Pd.]
Hammond Postulate:
The T.S. * resembles the "stable" species that is nearest in free energy

→ Endergonic Run: TS* resembles product

→ Exergonic Run: TS* resembles reactants

Therefore, to rate of run, more carbocation 
more stable!!
→ lower ΔG*!! → faster run!

What stabilizes a carbocation? Carbon substitution!

\[
\begin{align*}
R^1C^+R & > R^2C^+H & > R^3C^+H & > R^4C^+H \\
3^\circ & > 2^\circ & > 1^\circ & \text{methyl}
\end{align*}
\]
(tertiary) (secondary) (primary)

*: alkyl groups are more electron-releasing 
than a hydrogen atom! e- donating

Why? * Inductive effects
- through bond (σ system) donation

* Hyperconjugation

\[
\begin{align*}
R\cdots\sigma^* & \quad R\cdots\sigma^* \\
\overrightarrow{R}C\cdots\sigma^* & \quad \overrightarrow{R}C\cdots\sigma^* \\
R & \quad R
\end{align*}
\]

controversial concept!
Stereochemistry of $S_N^1$ Reactions

$R^+\rightarrow R^-$

Nuc can attack either side →

Carbocation is planar → loses any stereochem. info

*This distinction is an excellent way to det. $S_N^1$ vs $S_N^2$ mechanisms.

DISCUSSING THE EXAM:

Mean: 72.3  High: 99
Median: 75  Low: 15

Approx. grades:

A > 90
B > 76
C > 65
D > 50

If you scored below a 50, be sure to attend discussion, do homework, etc!!!
Things to go over:

- Correct: [Structural formula]
- Incorrect: [Structural formula]

- Drawing chain cyclohexane!! Practice!!