Learning Objective

- distinguish 1st or 2nd order elimination reactions

Elimination reactions of alkyl halides can occur via the bimolecular E2 mechanism or unimolecular E1 mechanism as shown in the diagram below.

Comparing E1 and E2 mechanisms

When considering whether an elimination reaction is likely to occur via an E1 or E2 mechanism, we really need to consider three factors:

1) **The base**: strong bases favor the E2 mechanism, whereas, E1 mechanisms only require a weak base.

2) **The solvent**: good ionizing solvents (polar protic) favor the E1 mechanism by stabilizing the carbocation intermediate.

3) **The alkyl halide**: primary alkyl halides have the only structure useful in distinguishing between the E2 and E1 pathways. Since primary carbocations do not form, only the E2 mechanism is possible.

<table>
<thead>
<tr>
<th>Reaction Parameter</th>
<th>E2</th>
<th>E1</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkyl halide structure</td>
<td>tertiary &gt; secondary &gt; primary</td>
<td>tertiary &gt; secondary &gt;&gt;&gt;&gt; primary</td>
</tr>
<tr>
<td>nucleophile</td>
<td>high concentration of a strong base</td>
<td>weak base</td>
</tr>
<tr>
<td>mechanism</td>
<td>1-step</td>
<td>2-step</td>
</tr>
<tr>
<td>rate limiting step</td>
<td>anti-coplanar bimolecular transition state</td>
<td>carbocation formation</td>
</tr>
</tbody>
</table>
rate law \[ \text{rate} = k[R-X][\text{Base}] \]

rate = \( k[R-X] \)

stereochemistry
retained configuration mixed configuration

solvent not important polar protic

Exercises

1. Predict the dominant elimination mechanism (E1 or E2) for each reaction below. Explain your reasoning.

![Reaction A](image)

\[ \text{CH}_3\text{CH}_2\text{O}^- \text{ ethanol} \]

b) ![Reaction B](image)

\[ \text{ethanol heat} \]

2. Which one of the following groups of compounds would eliminate \( \text{HCl} \) most readily on reaction with potassium hydroxide? Explain your reasoning, draw the bond-line structure and give the IUPAC name of the product.

a) \( \text{(CH}_3)_3\text{CCl} \text{ CH}_3\text{CH}_2\text{CH}_2\text{Cl} \text{ CH}_3\text{CH(Cl)CH}_2\text{CH}_3 \)

b) \( \text{(CH}_3)_3\text{CCH}_2\text{Cl} \text{ (CH}_3\text{)_2CHCH}_2\text{Cl} \)

c) \( \text{(CH}_3)_3\text{CCCH}_2\text{Cl} \text{ (CH}_3\text{)_2CHCH}_2\text{Cl} \)

c) \( \text{Cl} \text{ Cl} \)

3. Specify the reaction conditions to favor the indicated elimination mechanism.
1. a) E2 reaction b/c secondary alkyl halide with a strong base.

b) E1 reaction b/c tertiary alkyl halide with a weak base.

2. a) 2-methylprop-1-ene

E1-butyl chloride will react faster b/c it is a tertiary alkyl halide reacting with a strong base via the E2 mechanism.

b) 3-methylbut-1-ene

1-chloro-3-methyl butane will react faster since both reactants are primary alkyl halides and the reaction conditions favor the E2 mechanism; the reactant with less steric hindrance at the beta-hydrogen will react faster.

c) cyclohexene

The alkyl halide b/c aryl halides cannot undergo elimination reactions under these conditions.
3. a) strong base, such as hydroxide, an alkoxide, or equivalent
   b) water or alcohol or equivalent weak base with heat
   c) strong base, such as hydroxide, an alkoxide, or equivalent