Chemistry 209
The Amylenes: 2-Methyl-2-Butene
Lecture Outline

1. Purpose of the Experiment
2. Preparation of Alkenes from Alcohols
3. Elimination Reactions (Zaitsev’s Rule)
4. Mechanism of Acid Catalyzed Dehydration of Alcohols
5. Test for Unsaturation
6. Procedure
7. Percent yield
Purpose

1. To review the *synthesis* of alkenes.
2. To *synthesize* an alkene (2-methyl-2-butene) by *acid catalyzed dehydration* of an alcohol (2-methyl-2-butanol).
3. To apply the techniques of *extraction*, *drying* and *distillation* in the *purification* of the alkene.
4. To *calculate* the *percent yield* of the alkene.
5. To *test* the alkene for *unsaturation*. 
Theory

Amylenes is a generic name given for alkenes with general formula $\text{C}_5\text{H}_{10}$

2-Methyl-2-butene is prepared by the acid catalyzed dehydration of the alcohol 2-methyl-2-butanol (t-amyl alcohol)

*Elimination* by alcohol dehydration is readily accomplished by heating in the presence of an acid catalyst such as sulfuric or phosphoric.

![Chemical reaction](attachment:reaction.png)

2-Methyl-2-butanol $\xrightarrow{\text{H}_2\text{SO}_4, 80^\circ\text{C}}$ 2-Methyl-2-butene + 2-Methyl-1-butene

(major) (minor)
Dehydration of Alcohols

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 160^\circ\text{C}} \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{C} = \text{C} - \text{OH} \xrightarrow{\text{H}_2\text{SO}_4, 140^\circ\text{C}} \text{(79-87%)}
\]

\[
\text{H}_3\text{C} - \text{C} - \text{OH} \xrightarrow{\text{H}_2\text{SO}_4, \text{heat}} \text{(82%)}
\]
Relative Reactivity

Primary:
Least reactive

Tertiary:
Most reactive
Elimination reactions produce more than one alkene, however only one predominates in accordance with Zaitsev’s rule.

**Zaitsev’s rule**: When two or more alkenes are capable of being formed by an elimination reaction, the one with the more highly substituted double bond (the more stable alkene) is the *major* product.
The Zaitsev Rule

When elimination can occur in more than one direction, the principal alkene is the one formed by loss of $H$ from the $\beta$ carbon having the fewest hydrogens. This will lead to the formation of the more substituted double bond.

![Diagram showing the Zaitsev Rule](image-url)
A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be regioselective.
Mechanism of Acid Catalyzed Dehydration E1

1\textsuperscript{st} step in the mechanism is the \textit{protonation} of the alcohol by the acid to form the alkylloxonium ion.

2\textsuperscript{nd} step is the dissociation of the alkylloxonium ion by loss of water to form a tertiary \textit{carbocation}, the rate determining step.

3\textsuperscript{rd} step is the deprotonation of the carbocation to give a mixture of alkenes.

Relative ease of dehydration of alcohols:

\[ 3^\circ > 2^\circ > 1^\circ \]
2-methyl-2-butanol + $H_3O^+$ → Alkyl oxonium ion

Step (1) → Step (2) → Step (3)

2-methyl-2-butene (Major) + 2-methyl-1-butene (Minor)
Test for Unsaturation

1. Reaction with Br₂/CCl₄

\[ C = C + \text{Br}_2/\text{CCl}_4 \rightarrow C - C \]

2. Reaction with aqueous KMnO₄ (Baeyer’s test)

\[ C = C + \text{KMnO}_4 \rightarrow C - C + \text{MnO}_2 \]
Procedure

1. **Synthesis of the alkene.**
   - Prepare a 1:2 sulfuric acid-water mixture (Add acid to water) in a 100 mL r.b. flask.
   - Add 14 mL (0.125 mol) of t-amyl alcohol with swirling and cooling.
   - Distil the mixture over a *steam* bath (~25 min).
   - Collect the alkene in a 125 mL erlenmeyer flask fitted with a cotton plug and placed in an *ice bath*.
   - **Clean** and **dry** the distillation setup for use later in the final purification distillation.
2. Purification of the crude alkene.

The crude alkene contains: water, traces of acid and ether (a by product of the reaction)

- Transfer the cooled alkene into a separatory funnel
- Add 5 mL of 10% dilute NaOH (to remove the acid)
  - observe two layers
  - remove the aqueous layer (lower)
  - pour the upper organic layer through the mouth of the funnel into a small, clean, dry Erlenmeyer flask.
➢ Add anhydrous CaCl$_2$ (0.5 g), cover and allow the flask to stand with occasional shaking and cooling until the alkene is **dry** (*absence of turbidity*)

CaCl$_2$ + 2H$_2$O $\rightarrow$ CaCl$_2$.2H$_2$O

➢ Decant into a dry 50 mL r.b. flask

➢ Distil and collect the fraction boiling between 37°C-43°C. (b.p. = 38.5°C)

➢ Weigh the product

**3. Test for unsaturation**

Pour few mL of the alkene into two test tubes

➢ Add to the first a few drops of Br$_2$/CCl$_4$ solution

➢ Add to the second a few drops of KMnO$_4$ solution

Record your observations
4. Calculate percent yield

\[
\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100
\]

*Theoretical* yield is calculated from the stoichiometry of the reaction and the number of moles used, in this experiment the mole ratio is 1:1

\[\Rightarrow\] Theoretical yield of *alkene*

\[= \# \text{ of moles} \times \text{molar mass}\]