ACID-CATALYZED DEHYDRATION OF 2-METHYLCYCLOHEXANOL

Douglas G. Balmer

(T.A. Mike Hall)

Dr. Dailey

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Introduction: The purpose of this experiment is to acid-catalyze the dehydration of 2-methyl cyclohexanol. The product mixture will contain 1-methylcyclohexene and 3-methylcyclohexene. A 2:1 ratio in favor of 3-methylcyclohexene would be statistically expected based on the number of β hydrogens (Fig. 1). The actual ratio of products will be measured using gas-liquid chromatography, G.C.

Russian scientist, Alexander Saytzeff, came to the conclusion that the most highly substituted alkene usually predominates in addition reactions. Since 1-methylcyclohexene has three substituents on the double bond and 3-methylcyclohexene only has two substituents, Saytzeff’s rule predicts that 1-methylcyclohexene will predominate (Fig. 2).

FIGURE 1 Statistically, 3-methylcycloexene has twice the probability of forming as 1-methylcyclohexene.

FIGURE 2 Saytzeff’s rule predicts that 1-methylcyclohexene will predominate because it is more highly substituted.
Main Reaction and Mechanism: The first step of the mechanism involves the hydronium ion. The hydronium ion is produced when sulfuric acid deprotonates in water. The alcohol’s oxygen acts as a Lewis base and donates electrons to a hydrogen on the hydronium ion. This forms an oxonium ion. The oxonium ion cleaves from the cyclohexane ring, forming a 2° carbocation. The water acts as a Lewis base as electrons are donated to a β-hydrogen. The β-hydrogen transfers its electrons to the ring forming a methylcyclohexene. Sayzteff’s rule predicts that 1-methylcyclohexene will predominate.
FIGURE 3 The acid-catalyzed dehydration mechanism of 1-methylcyclohexanol. The major product is 1-methylcyclohexene and the minor product is 3-methylcyclohexene.

Table of Reactants:

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>cis and trans 2-methylcyclohexanol C₇H₁₄O</td>
<td><img src="image" alt="Structure" /></td>
<td>114.187</td>
<td>5.0mL</td>
<td>1</td>
<td>ρ = 0.93g/mL, m.p. = -38˚C, f.p. = 58˚C, b.p. = 163-166˚C</td>
</tr>
<tr>
<td>sulfuric acid H₂SO₄</td>
<td>---</td>
<td>98.0734</td>
<td>9M</td>
<td>catalyst</td>
<td>ρ = 1.84g/mL, m.p. = 3˚C, b.p. = 280˚C, ρᵥap = 3.4</td>
</tr>
</tbody>
</table>

Table of Products:

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>1-methylcyclohexene C₇H₁₂</td>
<td><img src="image" alt="Structure" /></td>
<td>96.1718</td>
<td>1/3 (40.7mmol)</td>
<td>1</td>
<td>ρ = 0.811g/mL, m.p. = -120˚C, f.p. = -3˚C, b.p. = 110˚C</td>
</tr>
<tr>
<td>3-methylcyclohexene C₇H₁₂</td>
<td><img src="image" alt="Structure" /></td>
<td>96.1718</td>
<td>2/3 (40.7mmol)</td>
<td>1</td>
<td>ρ = 0.801g/mL, m.p. = -124˚C, f.p. = -3˚C, b.p. = 104˚C</td>
</tr>
</tbody>
</table>

Yield Data: A volume of 5.0mL corresponds to 40.7mmol. The mass of the methylcyclohexene isomers produced should be 3.91g (Eq.1). The actual amount of product obtained was 1.86g.

The percent yield for the reaction was 47.6%.

\[
40.7\text{mmol alcohol} \times \frac{1}{1} \text{molar ratio} \times \frac{96.1718\text{g}}{1\text{mol}} = 3.91\text{g alkene}
\] (1)
Experimental Procedure: A reflux apparatus was assembled with a 25mL round-bottom flask and magnetic stirbar (Fig.4). 2-methylcyclohexanol (5.0mL) and 9M sulfuric acid (3.5mL) were added to the reaction flask. The Thermowell heater was adjusted to 70V for a reflux rate of 1 drop every 1-2 seconds. A 10mL graduated cylinder, cooled in an ice bath, was used to collect the distillate. The distillate’s volume and temperature were recorded (Tbl. 1, Fig. 5). It took approximately 60 minutes for the reflux to complete.

![Reflux apparatus with a 10mL graduated cylinder cooled in an ice bath for collection.](image)

**TABLE 1** Volume and head temperature data for the distillate.

<table>
<thead>
<tr>
<th>Distillate Volume (mL)</th>
<th>Head Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>78.8</td>
</tr>
<tr>
<td>0.5</td>
<td>79.0</td>
</tr>
<tr>
<td>1.0</td>
<td>79.1</td>
</tr>
<tr>
<td>1.5</td>
<td>79.1</td>
</tr>
<tr>
<td>2.0</td>
<td>79.1</td>
</tr>
<tr>
<td>2.5</td>
<td>75.0</td>
</tr>
<tr>
<td>3.0</td>
<td>75.9</td>
</tr>
<tr>
<td>3.78</td>
<td>88.0</td>
</tr>
</tbody>
</table>
FIGURE 5  Head temperature vs. distillate volume graph.

The distillate was transferred to a separatory funnel and washed with 10mL of water. The bottom aqueous layer was clear, and the top organic layer was cloudy-white. Lots of the organic layer formed droplets on the walls of the separatory funnel. The aqueous layer was acidic, because it turned blue litmus red. The aqueous layer was separated, and the organic layer was washed with 10mL of 3N NaOH. The bottom aqueous layer was a little cloudy, and the top organic layer was relatively clear. No organic droplets formed on the walls of the separatory funnel. The acid was neutralized, because the aqueous layer turned red litmus blue. The aqueous layer was separated, and the organic layer was washed with 10mL of brine solution. Both of the layers were very clear, and there was a nice separation between the two. The aqueous layer was separated and the organic layer was drained into a 25mL Erlenmeyer flask. Several spatula scoops of calcium chloride were placed in the corked Erlenmeyer flask to dry the organic layer. The dry, organic layer was transferred by pipette to a tared vial. The mass of the methylcyclohexene isomers was 1.86g.
A bromine unsaturation test was performed on the product, cyclohexane, and cyclohexene. Two drops of each sample and ten drops of methylene chloride were transferred to separate test tubes. A 0.1M solution of bromine in methylene chloride was added dropwise until a light orange persisted. A positive test was indicated by the rapid disappearance of the orange color. The results of the bromine unsaturation tests are shown in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Result of adding bromine solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexene isomers</td>
<td>rapidly cleared; positive for unsaturation</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>stayed orange; negative for unsaturation</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>rapidly cleared; positive for unsaturation</td>
</tr>
</tbody>
</table>

**TABLE 2** Bromine unsaturation test results.

A Baeyer unsaturation test was performed on the product, cyclohexane, and cyclohexane. Two drops of each sample and 2mL of 95% ethanol were transferred to separate test tubes. Several drops of purple 0.1M KMnO$_4$ were added to each test tube. A positive test was indicated by the formation of a brown precipitate, MnO$_2$. The results of the Baeyer unsaturation tests are shown in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Result of adding bromine solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylcyclohexene isomers</td>
<td>turned brown and cloudy; positive for unsaturation</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>stayed purple and transparent; negative for unsaturation</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>turned brown and cloudy; positive for unsaturation</td>
</tr>
</tbody>
</table>

**TABLE 3** Baeyer unsaturation test results.

The products were analyzed using GC #7. A 2.5µL sample was injected into column A which was set at the following conditions: + polarity, 100mA current, 77°C column temperature, 125°C detector temperature, and 125°C injector temperature.
Properties of Products:

A 1.86g sample of methycyclohexene isomers was collected. The sample consisted of 67.712% 1-methycyclohexene and 32.288% 3-methycyclohexene (Fig. 6).

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass (g)</th>
<th>Bromine Test</th>
<th>Baeyer Test</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>methycyclohexene isomers</td>
<td>1.86</td>
<td>positive</td>
<td>Positive</td>
<td>clear liquid</td>
</tr>
</tbody>
</table>

**FIGURE 6** GC trace of the methycyclohexene sample. 3-methycyclohexene had the shortest retention time (top) and 1-methycyclohexene had the longest retention time (bottom).
Significant Side Reactions: The methylcyclohexene isomers were distilled for two reasons. First, by removing the product, the equilibrium between the alcohol and alkene was shifted toward the alkene. Secondly, the alkene could react with the carbocation to form a polymer (Fig. 7).

![Figure 7: Polymerization of 1-methylcyclohexene with the 2° carbocation.]

The possibility for a third alkene does exist. If the 2° carbocation shifted a hydride ion from the 3° location, a 3° carbocation could form. If this carbocation became an alkene, it could form 1-methylcyclohexene and methylene cyclohexane (Fig. 8). It would be hard to distinguish between 3-methylcyclohexene and methylenecyclohexane since their boiling points are 104°C and 103°C, respectively.
**FIGURE 8** Hydride shift to form a 3° carbocation. The 3° carbocation can form 1-methylcyclohexene and

**Method of Purification:** The products were purified according to Figure 9. The distilled methylcyclohexene isomers were washed with water to absorb any sulfuric acid. The sodium hydroxide wash was used to neutralize any remaining sulfuric acid left in the organic layer. The brine wash was used to help separate remaining water from the organic layer. Finally, calcium chloride was used to dry the organic layer.
FIGURE 9 Purification of methylcyclohexene isomers.

Conclusions: The results support that the acid-catalyzed dehydration of 2-methycyclohexanol was successful. The GC percentages support Sayzteff’s rule; the more highly substituted alkene was the major product. 1-Methycyclohexene formed 67.712% of the product mixture and 3-methylcyclohexene formed 32.288% of the product mixture. Both the bromine and the Baeyer unsaturation tests were positive for unsaturation. The product ratio was relatively close to the 75%, 25% ratio predicted using thermodynamic stability and the free energy equation, \[ \Delta G = RT \ln K. \]
Answers to Assigned Questions:  Page 289-291 (1,21)

1) Why is the boiling point of the parent alcohol higher than that of the product alkene?

   The 2-methylcyclohexanol has the higher boiling point because it has more intermolecular forces. It has the ability to hydrogen bond, whereas the methylcyclohexene isomers are nonpolar and only have London dispersion forces.

21) Provide a detailed mechanism for the acid-catalyzed dehydration of cyclohexanol.
Additional Question) What is the predicted product ratio between 1-methylcyclohexene and 3-methylcyclohexene using Chem3D?

\[
\begin{array}{ll}
\text{Torsion: } & -0.4902 \text{kcal/mol} \\
\text{Non-1,4 VDW: } & -0.9801 \text{kcal/mol} \\
\text{1,4 VDW: } & 4.4087 \text{kcal/mol} \\
\text{Dipole/Dipole: } & 0.1869 \text{kcal/mol} \\
\text{Total: } & 3.9936 \text{kcal/mol}
\end{array}
\quad
\begin{array}{ll}
\text{Torsion: } & 0.3631 \text{kcal/mol} \\
\text{Non-1,4 VDW: } & -1.1340 \text{kcal/mol} \\
\text{1,4 VDW: } & 4.8038 \text{kcal/mol} \\
\text{Dipole/Dipole: } & 0.1099 \text{kcal/mol} \\
\text{Total: } & 5.0287 \text{kcal/mol}
\end{array}
\]

\[
5.0287 \text{kcal/mol} - 3.9936 \text{kcal/mol} = 1.0351 \text{kcal/mol} = 4330.8 \text{J/mol}
\]

\[
K_{eq} = \frac{[3\text{-methylcyclohexene}]}{[1\text{-methylcyclohexene}]}
\]

\[
\Delta G = RT \ln K
\]

\[
4330.8 \text{J/mol} = 8.3145 \text{J/molK} \times 373 \text{K} \times \ln (K)
\]

\[
\ln (K) = -1.40
\]

\[
K = 0.25
\]

Based on thermodynamics, the product ratio should be 75% 1-methylcyclohexene and 25% 3-methylcyclohexene. The actual product ratio was relatively close. It has a ratio of 67.712% 1-methylcyclohexene and 32.288% 3-methylcyclohexene.