Acid-Catalyzed Hydration of Alkenes

The reaction is acid catalyzed; typical hydration medium is 50% H$_2$SO$_4$, 50% H$_2$O.

Follows Markovnikov's Rule

Mechanism

Involves a carbocation intermediate, which is the reverse of acid-catalyzed dehydration of alcohols to alkenes.

Step 1: Protonation of double bond
Step (2) Capture of carbocation by water

\[ \text{H}_3\text{C} - \text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C} - \text{CH}_2\text{O}^- \]

Fast

CH\text{\textsubscript{3}}\text{CH}_3 C\text{\textsubscript{\textbullet}}\text{CH}_3

Step (3) Deprotonation of oxonium ion

\[ \text{CH}_3\text{C} - \text{CH}_2\text{O}^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C} - \text{CH}_2\text{OH} + \text{H}_3\text{O}^+ \]

Fast

Relative Rates

**Acid-catalyzed hydration**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>1.0</td>
</tr>
<tr>
<td>Propene</td>
<td>1.6 x 10^8</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>2.5 x 10^11</td>
</tr>
</tbody>
</table>

The more stable the carbocation, the faster it is formed, and the faster the reaction rate.

Principle of Microscopic Reversibility

In an equilibrium process, the same intermediates and transition states are encountered in the forward direction and the reverse, but in the opposite order.

**Hydration-Dehydration Equilibrium**

How do we control the position of the equilibrium and maximize the product?
**Le Chatelier’s Principle**

A system at equilibrium adjusts so to minimize any stress applied to it.

For the hydration-dehydration equilibria, the key stress is water.

Adding water pushes the equilibrium toward more product (alcohol).

Removing water pushes the equilibrium toward more reactant (alkene).

---

**Le Chatelier’s Principle**

At constant temperature and pressure a reaction proceeds in a direction which is spontaneous or decreases free energy (G).

The sign of G is always positive, but ΔG can be positive or negative.

\[ \Delta G = G_{\text{products}} - G_{\text{reactants}} \]

Spontaneous when \( \Delta G < 0 \)

---

**Le Chatelier’s Principle**

For a reversible reaction:

\[ aA + bB \leftrightarrow cC + dD \]

The relationship between \( \Delta G \) and \( \Delta G^\circ \) is:

\[ R = 8.314 \text{ J/(mol.K)} \text{ and } T \text{ is the temperature in } K \]

---

**Le Chatelier’s Principle**

At equilibrium \( \Delta G = 0 \) and the following becomes true:

Substituting \( K_{eq} \) into the previous equation gives:

\[ \Delta G^\circ = -RT \ln K_{eq} \]

Reactions for \( \Delta G^\circ \) positive are endergonic and for \( \Delta G^\circ \) negative are exergonic.

---

**Synthesis**

Suppose you wanted to prepare 1-decanol from 1-decene?

\[ \text{OH} \]

Needed: a method for hydration of alkenes with a regioselectivity opposite to Markovnikov’s rule.
Two-step reaction sequence called hydroboration-oxidation converts alkenes to alcohols with a regiochemistry opposite to Markovnikov’s rule.  

**Hydroboration Step**  
\[
\text{C} = \text{C} + \text{H}_2\text{BH}_3 \rightarrow \text{H} - \text{C} - \text{C} - \text{BH}_3
\]

Hydroboration can be viewed as the addition of borane (\(\text{BH}_3\)) to the double bond. But \(\text{BH}_3\) is not the reagent actually used.

**Hydroboration reagents:**  
- Diborane (\(\text{B}_2\text{H}_6\)) normally used in an ether-like solvent called “diglyme.”  
- Borane-tetrahydrofuran complex (\(\text{H}_3\text{B-THF}\)).

**Oxidation Step**  
\[
\text{H} - \text{C} - \text{C} - \text{BH}_3 + \text{H}_2\text{O}_2, \text{HO}^- \rightarrow \text{H} - \text{C} - \text{C} - \text{OH}
\]

Organoborane formed in the hydroboration step is oxidized with hydrogen peroxide.

**Example**  
1. \(\text{BH}_3\), diglyme  
2. \(\text{H}_2\text{O}_2\), \(\text{HO}^-\)  

(93%)
Example

\[ \text{H}_2\text{C} \overset{\text{C}}{\text{C}} \text{CH}_3 \rightarrow \text{H}_2\text{C} \overset{\text{C}}{\text{C}} \text{CH}_3 \]

1. \text{B-THF}
2. \text{H}_2\text{O}\text{₂, HO⁻}

(98%)

Features of Hydroboration-Oxidation

hydration of alkenes
regioselectivity opposite to Markovnikov's rule
no rearrangement
stereospecific syn addition

Example

\[ \text{CH}_3 \text{CH} \overset{\text{C}}{\text{CH}} \text{CH}_3 \rightarrow \text{CH}_3 \text{CH} \overset{\text{C}}{\text{CH}} \text{OH} \]

1. \text{B}_2\text{H}_6, \text{diglyme}
2. \text{H}_2\text{O}\text{₂, HO⁻}

(82%)

Stereochemistry of Hydroboration-Oxidation

6.13

Features of Hydroboration-Oxidation

hydration of alkenes
regioselectivity opposite to Markovnikov's rule
no rearrangement
stereospecific syn addition

syn Addition

\[ \text{H} \begin{array}{c} \text{CH} \text{C} \text{CH} \text{CH}_3 \end{array} \rightarrow \text{H} \begin{array}{c} \text{CH} \text{C} \text{OH} \text{CH}_3 \end{array} \]

1. \text{B}_2\text{H}_6
2. \text{H}_2\text{O}\text{₂, NaOH}

only product is trans-2-methylcyclopentanol
(86%) yield
6.14 Mechanism of Hydroboration-Oxidation

1-Methylcyclopentene + BH₃
- syn addition of H and B to double bond
- B adds to least substituted carbon

Organoborane Intermediate

Add Hydrogen Peroxide
- OH replaces B on same side

trans-2-Methylcyclopentanol

6.15 Addition of Halogens to Alkenes
**General features**

Electrophilic addition to double bond forms a vicinal dihalide.

**Example**

\[
\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)_2 + \text{Br}_2 \xrightarrow{\text{CHCl}_3, \text{0}^\circ \text{C}} \text{CH}_2\text{CHCHCHCH}(\text{CH}_3)_2 \text{Br} - \text{Br}
\]

(100%)

**Scope**

Limited to Cl\(_2\) and Br\(_2\):
- F\(_2\) addition proceeds with explosive violence.
- I\(_2\) addition is endothermic; vicinal diiodides dissociate to an alkene and I\(_2\).

**6.16 Stereochemistry of Halogen Addition**

**Example**

\[
\text{trans-1,2-Dibromocyclopentane} \quad \text{80\% yield; only product}
\]

\[
\text{trans-1,2-Dichlorocyclooctane} \quad \text{73\% yield; only product}
\]
Mechanism of Halogen Addition to Alkenes: Halonium Ions

Br₂ is not polar, but it is polarizable.

Mechanism:
(1) formation of bromonium ion
(2) nucleophilic attack on bromonium ion by bromide

Relative Rates of Bromination

<table>
<thead>
<tr>
<th>Alkene</th>
<th>Relative Rate</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>H₂C=CH₂</td>
<td>1</td>
</tr>
<tr>
<td>Propene</td>
<td>CH₃CH=CH₂</td>
<td>61</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>(CH₃)₂C=CH₂</td>
<td>5400</td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td>(CH₃)₂C=CH(CH₃)₂</td>
<td>920,000</td>
</tr>
</tbody>
</table>

More highly substituted double bonds react faster. Alkyl groups on the double bond make it more "electron rich." No obvious explanation for anti addition provided by this mechanism.

Mechanism of Bromination

H₂C=CH₂ + Br₂ → BrCH₂CH₂Br

Formation of Bromonium Ion

Mutual polarization of electron distributions of Br₂ and alkene.

Cyclic bromonium ion
Electrons flow from alkene toward Br₂

π electrons of alkene displace Br⁻ from Br₂

Stereochemistry

attack of Br⁻ from side opposite C—Br bond of bromonium ion gives anti addition

trans-1,2-Dibromocyclopentane
80% yield; only product

Cyclopentene + Br₂

Bromonium ion
**6.18 Conversion of Alkenes to Vicinal Halohydrins**

Bromide ion attacks the bromonium ion from side opposite carbon-bromine bond.

**trans-Stereochemistry in vicinal dibromide**

Alkenes react with $X_2$ to form vicinal dihalides.

Alkenes react with $X_2$ in water to give vicinal halohydrins.

**Examples**

$$\ce{\text{C}==\text{C} + \text{X}_2 \rightarrow \text{X} - \text{C} - \text{C} - \text{X}}$$

$$\text{H}_2\text{C}==\text{CH}_2 + \text{Br}_2 \rightarrow \text{BrCH}_2\text{CH}_2\text{OH}$$

(70%)

$$\text{anti addition: only product}$$
bromonium ion is intermediate.

Water is nucleophile that attacks bromonium ion.

Mechanism:

Examples:

\[ H_2C=CH_2 + Br_2 \xrightarrow{H_2O} BrCH\text{CH}_2\text{CH}_2\text{OH} \] (70%)

Anti addition: only product.

Cyclopentene + Cl$_2$

Chloronium ion

Water attacks chloronium ion from side opposite carbon-chlorine bond.

trans-Stereochemistry in oxonium ion.
trans-2-Chlorocyclopentanol

Markovnikov’s rule applied to halohydrin formation: the halogen adds to the carbon having the greater number of hydrogens.

Explanation

Transition state for attack of water on bromonium ion has carbocation character; more stable transition state (left) has positive charge on more highly substituted carbon.