Chem 109 C
Bioorganic Compounds

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Chapter 22

- CATALYSIS
- INTRAMOLECULAR REACTIONS
- EXAMPLES WITH ENZYMES
Catalyst - a substance that

1. accelerates a reaction, and
2. is not changed or consumed

\[
\text{rate} = \frac{d[P]}{dt} = k[A][B]
\]

\[k = Ae^{-E_a/RT}\]

\[k = \text{rate constant}\]

• note: the reaction still takes place without the catalyst, but is very slow
Draw energy diagrams to compare and classify catalyzed and uncatalyzed reactions:

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- **Note**: The reaction rate is the rate of the **slowest step**.
Problem 1

Which of the following parameters would be different for catalyzed vs uncatalyzed reaction (review Section 5.13)

\[ \Delta G^\circ, \quad \Delta H^\ddagger, \quad E_a, \quad \Delta S^\ddagger, \quad \Delta H^\circ, \quad K_{eq} \]

\[ \Delta G^\ddagger, \quad \Delta S^\circ, \quad k_{rate} \]

**important fact:** the reaction rate is the rate of the slowest step
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**important fact:** the reaction rate is the rate of the slowest step
An Acid Catalyst Increases the Rate of a Reaction by Donating a Proton

*note: the reaction rate is the rate of the slowest step*
How an Acid Catalyzes the “First Slow Step”

The catalyst increases the electrophilicity of the carbonyl carbon (makes it more susceptible to nucleophilic addition).

A catalyst must increase the rate of a slow step.
How an Acid Catalyzes “the Second Slow Step”

The catalyst decreases the basicity of the leaving group (increases its propensity to leave).
Types of catalysis we will be looking at:

- *acid catalysis* [specific, general]
- *base catalysis* [specific, general]
- *nucleophilic catalysis*
- *metal-ion catalysis*
Two types of acid catalysis:

1. *specific*: first protonation, then slow step
Two types of acid catalysis:

2. general: protonation and slow step at the same time
PROBLEM 3

Are the slow steps here general-acid catalyzed or specific-acid catalyzed?
Again, two types of base catalysis:

1. **specific**: first deprotonation, then slow step
Again, two types of base catalysis:

2. general: deprotonation and slow step at the same time

PROBLEM 6

\[
\text{B: } \begin{array}{c}
\text{O} \\
\text{OCH}_3 \\
\text{O}
\end{array} \rightarrow \begin{array}{c}
\text{O} \\
\text{CH}_3\text{OH}
\end{array}
\]

\[
\text{B: } \begin{array}{c}
\text{O} \\
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\]
PROBLEM 4

The following reaction occurs by a general-acid catalyzed mechanism:

Propose a mechanism for this reaction
the catalyst is a nucleophile

\[
\text{CH}_3\text{CH}_2\text{Cl} + \text{HO}^- \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} + \text{Cl}^-
\]

Draw the mechanism [catalyzed and uncatalyzed]:
the catalyst is a nucleophile

\[
\text{phenyl acetate} + \text{H}_2\text{O} \xrightarrow{\text{imidazole}} \text{acetic acid} + \text{phenol}
\]

draw the mechanism [catalyzed and uncatalyzed]:

NUCLEOPHILIC CATALYSIS
the catalyst is a nucleophile

PRACTICE PROBLEM
Draw an approximate energy diagram for the above reaction and its uncatalyzed version