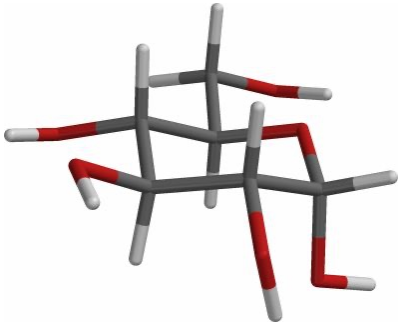

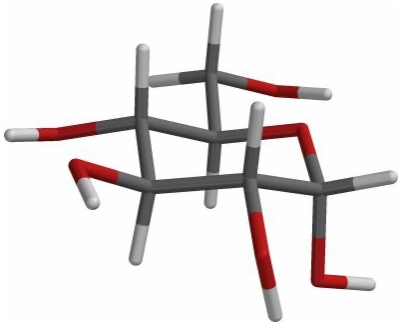

Chem 109 C
Bioorganic Compounds

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Chapter 22

- **CATALYSIS**
- **INTRAMOLECULAR REACTIONS**
- **EXAMPLES WITH ENZYMES**

CATALYSIS

Catalyst - a substance that

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

$$\text{rate} = d[P]/dt = k[A][B] \qquad k = Ae^{-E_a/RT}$$

k = rate constant

- **note: the reaction still takes place without the catalyst, but is very slow**

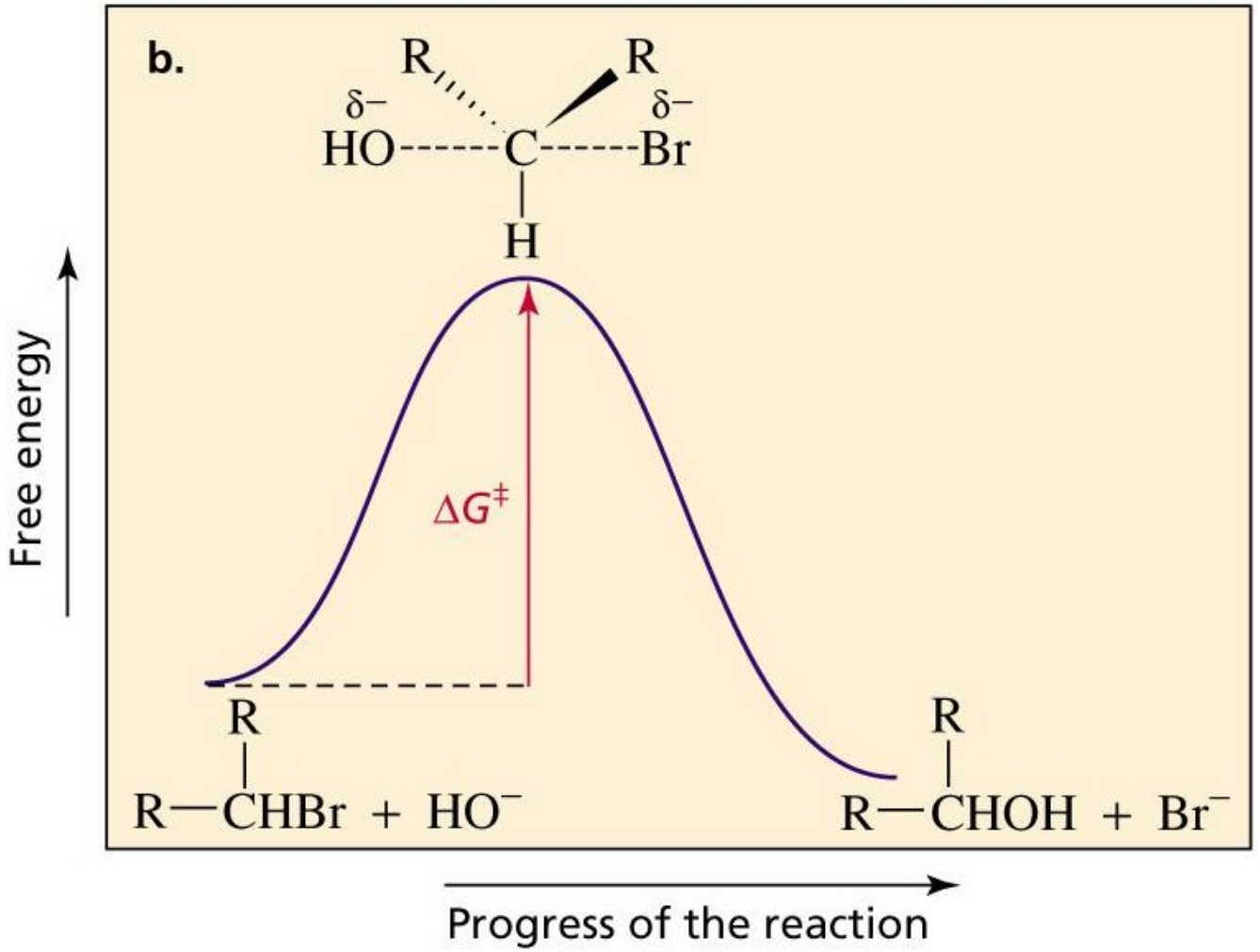
CATALYSIS

Draw energy diagrams *to compare and classify catalyzed and uncatalyzed reactions:*

note: the reaction rate is the rate of the slowest step

CATALYSIS

Draw energy diagrams *to compare and classify catalyzed and uncatalyzed reactions:*



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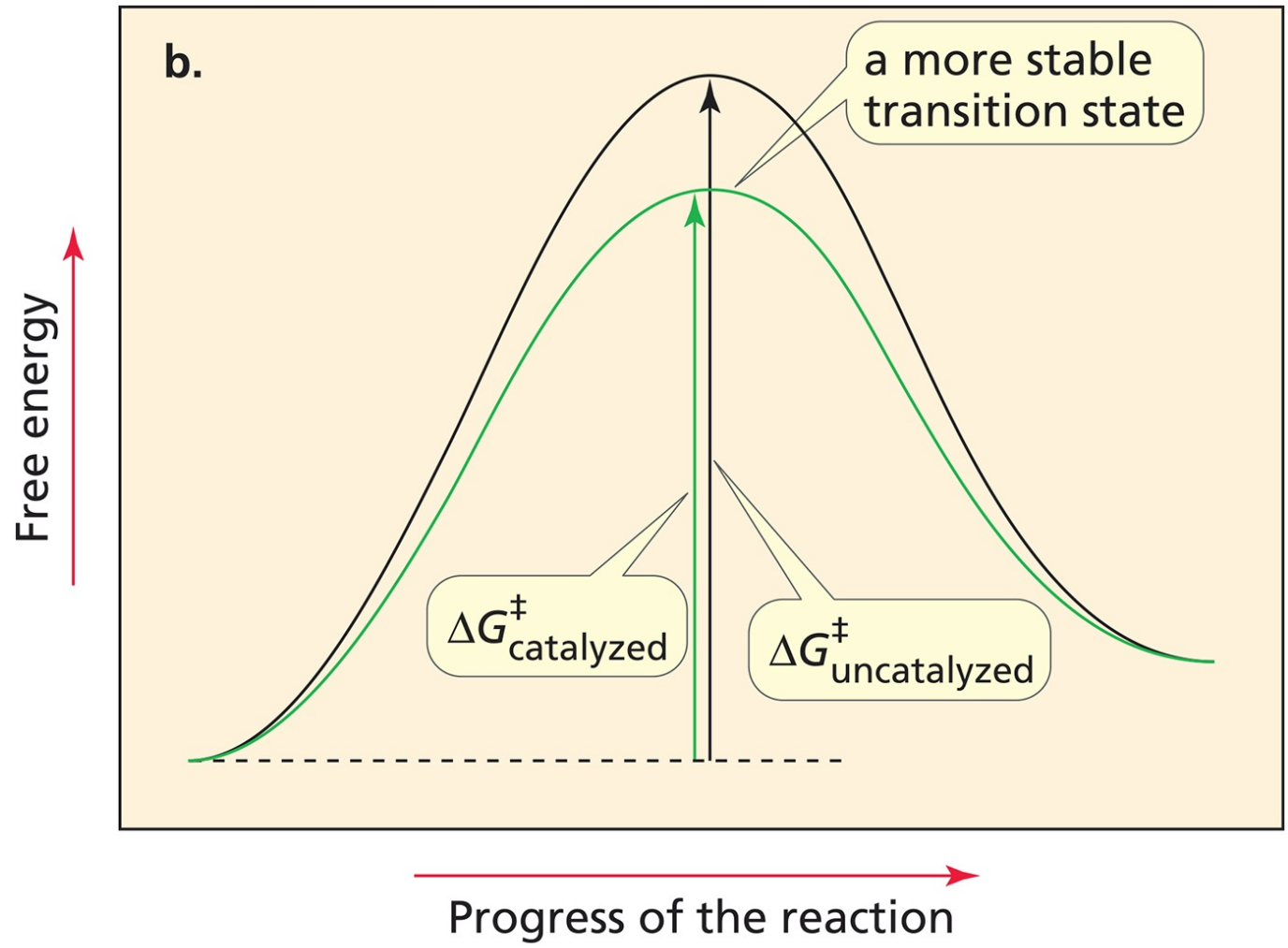
CATALYSIS

Draw energy diagrams *to compare and classify catalyzed and uncatalyzed reactions:*



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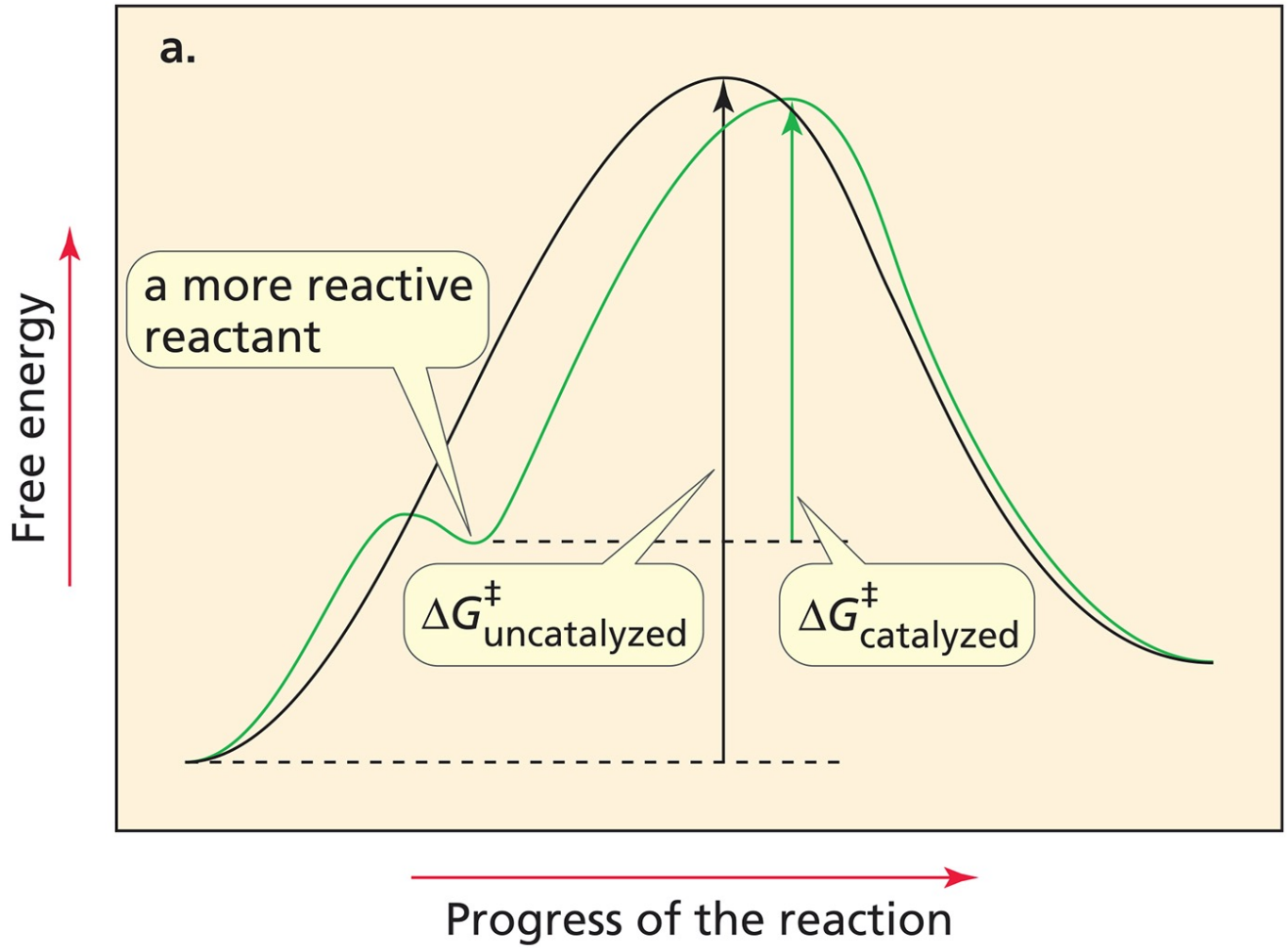
CATALYSIS

Draw energy diagrams *to compare and classify catalyzed and uncatalyzed reactions:*



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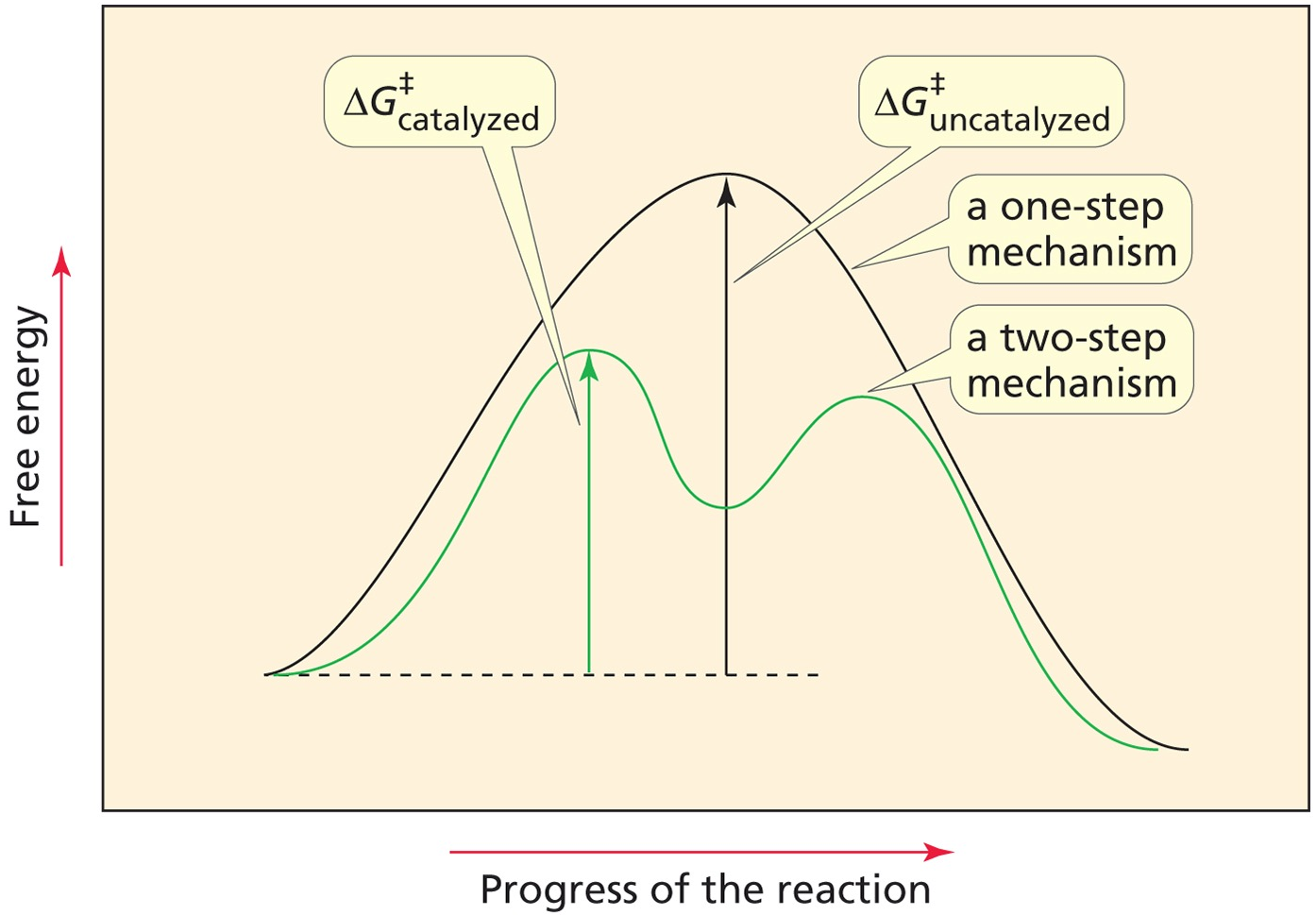
CATALYSIS

Draw energy diagrams *to compare and classify catalyzed and uncatalyzed reactions:*



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)

ΔG° , $\Delta H^\ddagger$, E_a, $\Delta S^\ddagger$, ΔH° , K_{eq}

$\Delta G^\ddagger$, ΔS° , k_{rate}

important fact: the reaction rate is the rate of the slowest step

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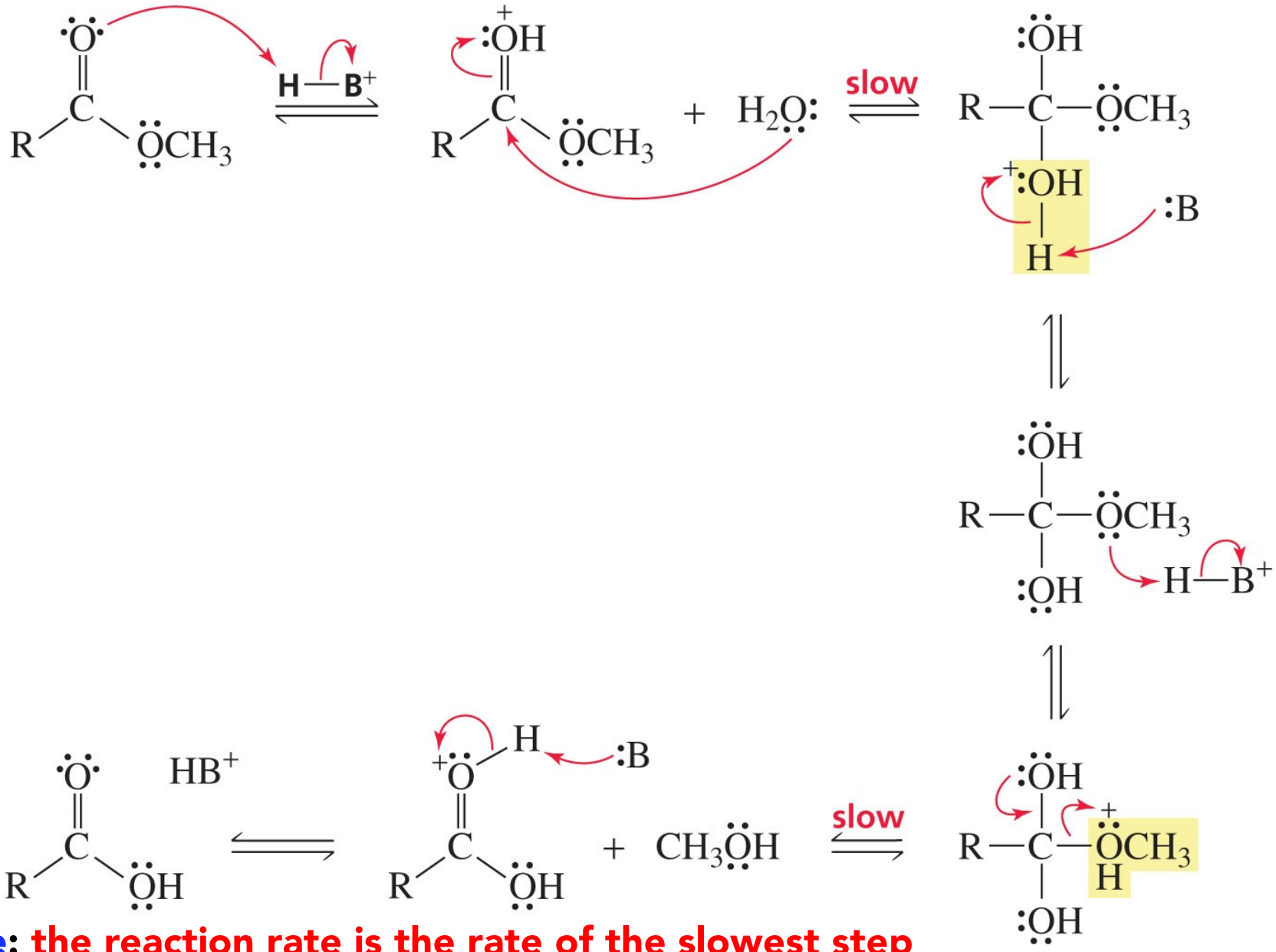
$\Delta G^\ddagger$, ΔS° , k_{rate}

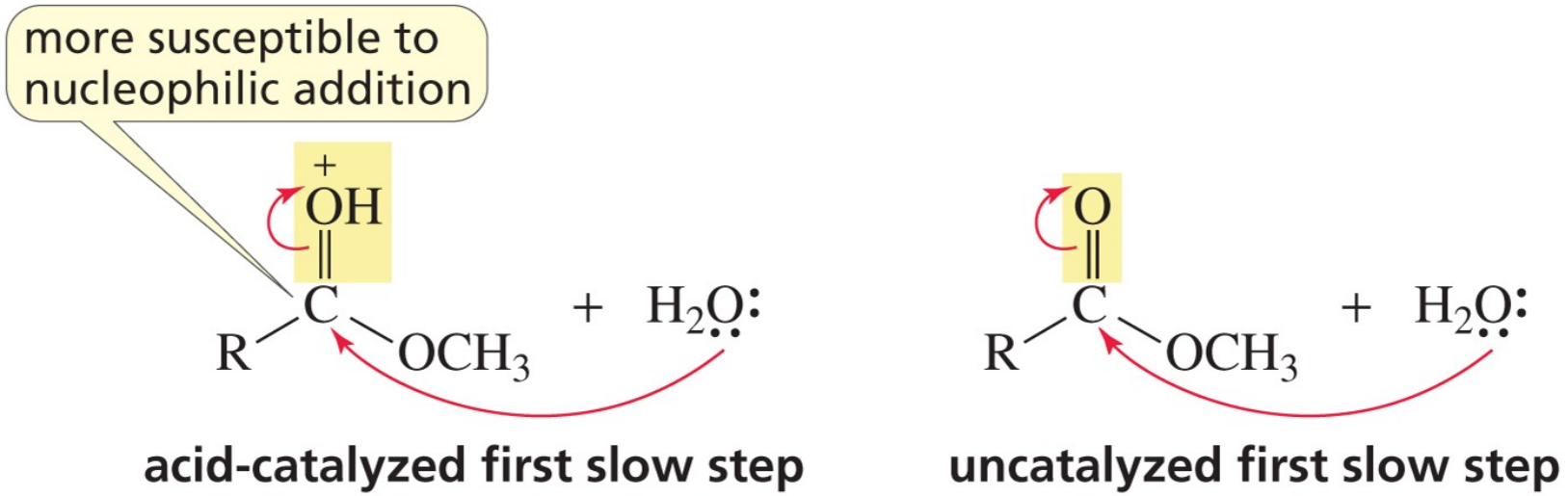
important fact: the reaction rate is the rate of the slowest step

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"

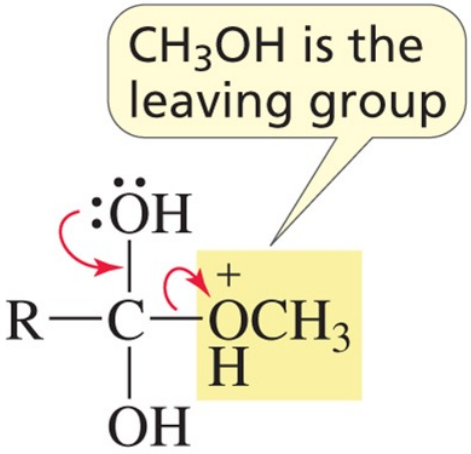


acid-catalyzed first slow step **uncatalyzed first slow step**

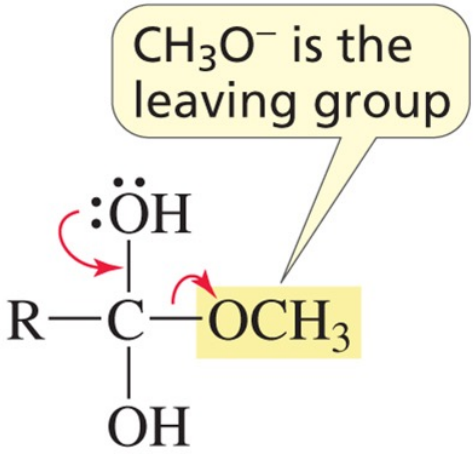
The catalyst increases the electrophilicity of the carbonyl carbon (makes it more susceptible to nucleophilic addition).

A catalyst must increase the rate of a slow step.

How an Acid Catalyzes “the Second Slow Step”



acid-catalyzed second slow step



uncatalyzed second slow step

The catalyst decreases the basicity of the leaving group (increases its propensity to leave).

CATALYSIS

Types of catalysis we will be looking at:

- ***acid catalysis*** **[specific, general]**
- ***base catalysis*** **[specific, general]**
- ***nucleophilic catalysis***
- ***metal-ion catalysis***

ACID CATALYSIS

Two types of acid catalysis:

1. specific: first protonation, then slow step

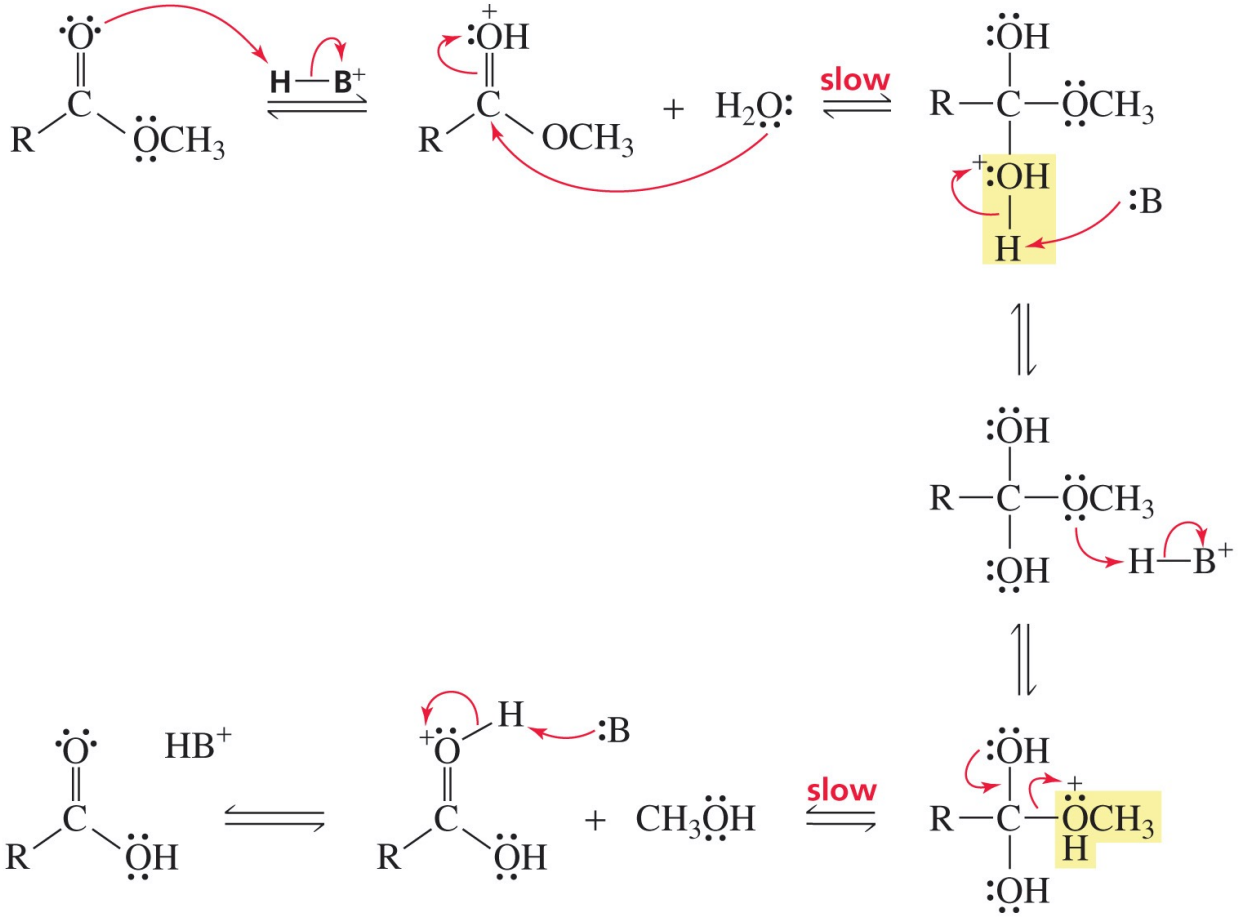
ACID CATALYSIS

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?



BASE CATALYSIS

Again, two types of base catalysis:

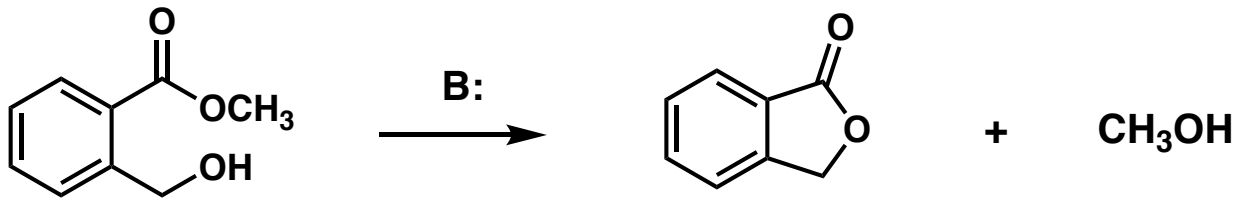
1. specific: first deprotonation, then slow step

BASE CATALYSIS

Again, two types of base catalysis:

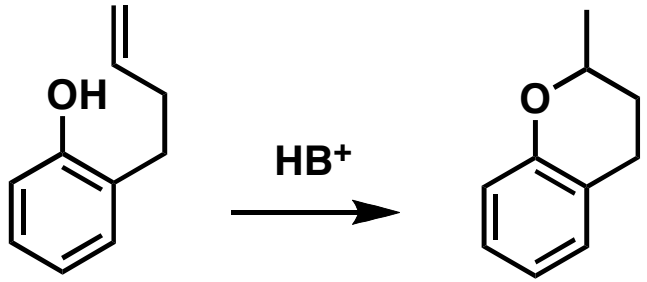
2. general: deprotonation and slow step at the same time

PROBLEM 6



PROBLEM 4

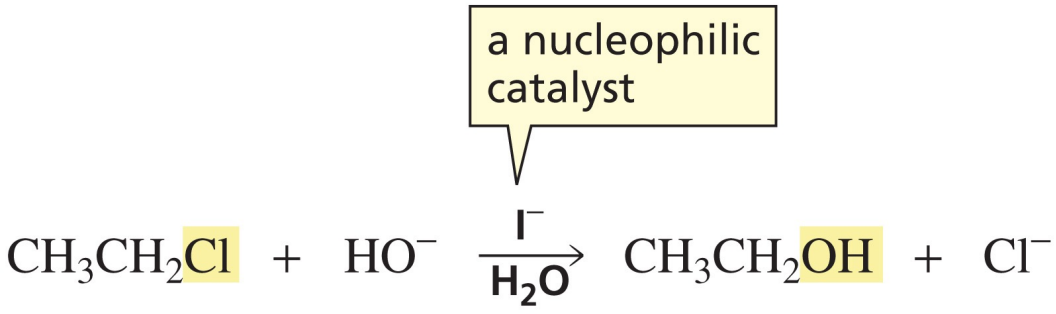
The following reaction occurs by a general-acid catalyzed mechanism:



Propose a mechanism for this reaction

NUCLEOPHILIC CATALYSIS

the catalyst is a nucleophile



Draw the mechanism [catalyzed and uncatalyzed]:

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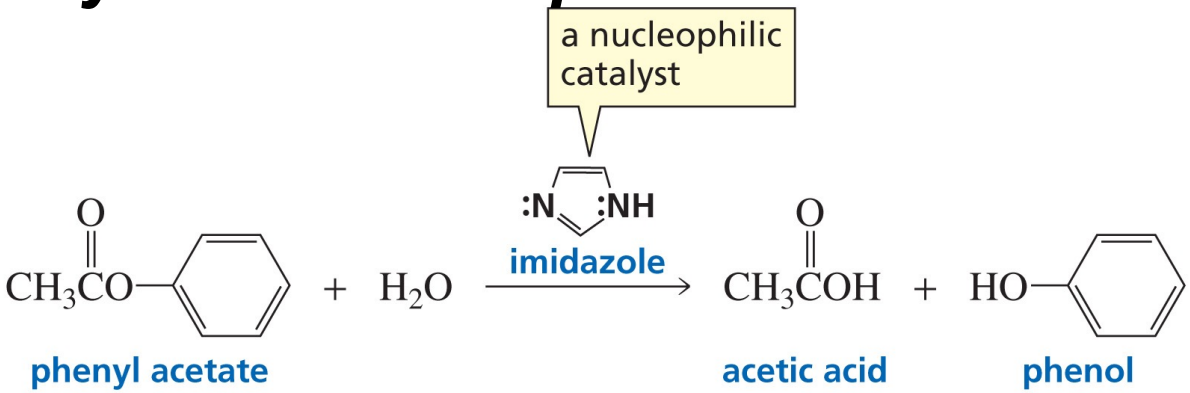

Draw the mechanism [catalyzed and uncatalyzed]:

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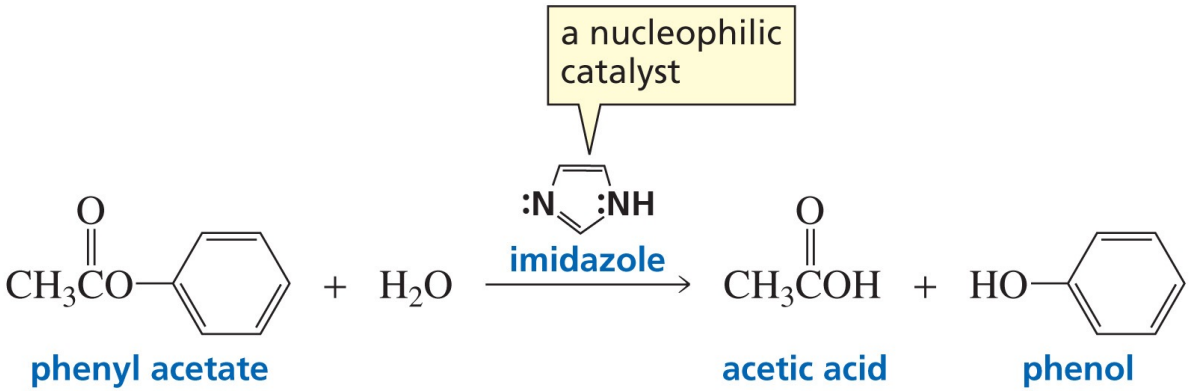

PRACTICE PROBLEM

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