Objective 6. Describe reaction mechanisms and relate mechanism to rate law and reaction energy diagram.

1. In Lab 1, you heated isoamyl alcohol with acetic acid in the presence of a sulfuric acid catalyst to make isoamyl acetate.

a. For each change in reaction condition, determine whether each quantity increases, decreases, or stays the same.

Change in Reaction Condition	Reaction Rate	Rate Constant	Activation Energy
Lower the temperature			
Use concentrated acetic acid solution			
Forget to add sulfuric acid			

b. Which change in reaction condition changes the reaction mechanism? Give reasons.

c. Draw a reaction energy diagram (plot energy on the y axis and progress of reaction (also called reaction coordinate) on the x axis) for this reaction with <u>and</u> without the catalyst. Label ΔH and the activation energy on your diagram.

2. You studied the Iodine Clock Reaction in Lab 3:

$IO_3^- + 3\ HSO_3^- \text{-->} I^- + 3\ SO_4^{2-} + 3\ H^+$

The rate law was determined by experiment to be: rate = k $[IO_3^-]\ [HSO_3^-]$

The reaction mechanism is the sequence of elementary steps by which bonds break and form going from reactants to intermediates to products.

a. The slowest step in a reaction mechanism is called the _______.

The rate of the slowest step should match the experimentally determined rate law. In other words, the rate of the slowest step in the iodine clock reaction is 1st order in IO_3^- and 1st order in HSO_3^-.

In a reaction mechanism, you can write a rate law for each elementary step. The order with respect to each reactant is based on the coefficient in the elementary step.

Here is a possible reaction mechanism for the iodine clock reaction and the rate law for each elementary step:

$IO_3^- + HSO_3^- \text{--->} I^- + O_2 + SO_4^{2-} + H^+$ rate of elementary step 1 = k $[IO_3^-]\ [HSO_3^-]$

$O_2 + 2HSO_3^- \text{--->} 2\ SO_4^{2-} + 2\ H^+$ rate of elementary step 2 = k $[O_2]\ [HSO_3^-]^2$

Compare the rate law for each elementary step to the experimental rate law (rate = k $[IO_3^-]\ [HSO_3^-]$). The rate law of the first elementary step matches the experimental rate law so this reaction mechanism is a possible mechanism for the iodine clock reaction. Since the rate law of the first elementary step matches the experimental rate law, the first elementary step is the rate determining step.

b. For each mechanism, write a rate law for <u>each</u> elementary step.

Mechanism A:

$IO_3^- \text{--->} IO^- + O_2$ rate of elementary step 1 =

$IO^- + HSO_3^- \text{--->} I^- + SO_4^{2-} + H^+$ rate of elementary step 2 =

$O_2 + HSO_3^- \text{--->} O + SO_4^{2-} + H^+$ etc.

$O + HSO_3^- \text{--->} SO_4^{2-} + H^+$

Mechanism B:

$IO_3^- + HSO_3^- \text{--->} IO_2^- + HSO_4^-$

$IO_2^- + HSO_3^- \text{--->} IO^- + HSO_4^-$

$IO^- + HSO_3^- \text{--->} I^- + HSO_4^-$

c. Add the elementary steps for each mechanism. Do you get the iodine clock reaction?

d. Which mechanism, A or B, is a possible mechanism for the iodine clock reaction? Give reasons.

3. Studies show that CFC's destroy the ozone layer. Another way that ozone in the upper atmosphere is destroyed is by high flying aircraft that produce NO:

$O_3\ (g) + NO\ (g) \text{---->} NO_2\ (g) + O_2\ (g)$. Rate = k $[O_3]\ [NO]$

It is colder in the upper atmosphere where this reaction occurs than on the surface of the Earth.

Four possible mechanisms for this reaction are shown below.

(i) $O_3 \text{--->} O_2 + O$
$O + NO \text{--->} NO_2$

(ii) $O_3 + NO \text{---->} NO_3 + O$
$NO_3 + O \text{---->} NO_2 + O_2$

(iii) $NO \text{--->} N + O$
$O + O_3 \text{---->} 2\ O_2$

O_2 + N ----> NO_2

(iv) O_3 + NO ----> NO_2 + O_2

a. For each mechanism, write a rate law for each elementary step.
b. Add the elementary steps for each mechanism. Do you get the overall reaction?
c. Which mechanism best fits the data? Give reasons. Which elementary step is the rate determining step?

4. You may have used hydrogen peroxide (H_2O_2) to disinfect a wound. H_2O_2 decomposes to water and O_2 and has an activation energy of 75 kJ/mole.

2 H_2O_2 ---> 2 H_2O + O_2

The rate law for the H_2O_2 decomposition without a catalyst is: rate = k $[H_2O_2]^2$
The rate law for the H_2O_2 decomposition with a I^- catalyst is: rate = k $[H_2O_2]$ $[I^-]$
A catalyst increases the reactoin rate, is involved in the reaction mechanism, is not used up in the reaction (it is regenerated in the reaction mechanism), and is not involved in the overall reaction.
a. Is the H_2O_2 decomposition reaction fast or slow? How do you know?
b. Does the activation energy change if temperature increases? If not, what changes?
c. Does the activation energy change if a catalyst is used?
d. Consider the two reaction mechanisms:

Mechanism (i): 2 H_2O_2 ---> 2 H_2O + O
2 O ---> O_2

Mechanism (ii): H_2O_2 + I^- ---> H_2O + IO^-
H_2O_2 + IO^- ---> H_2O + I^- + O_2

(i) For each mechanism, write a rate law for each elementary step.
(ii) Add the elementary steps for each mechanism. Do you get the H_2O_2 decomposition reaction?
(iii) Which mechanism fits the catalyzed H_2O_2 decomposition? Give reasons. Which elementary step is the rate determining step?
(iv) For the catalyzed H_2O_2 decomposition mechanism, in which elementary step is the catalyst regenerated?