

Objective 6. Quiz Practice Problems Solutions

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 and without the catalyst. Label ΔH and the activation energy on your diagram.

Answers:

a. Reaction rate changes with change in temperature or concentration.

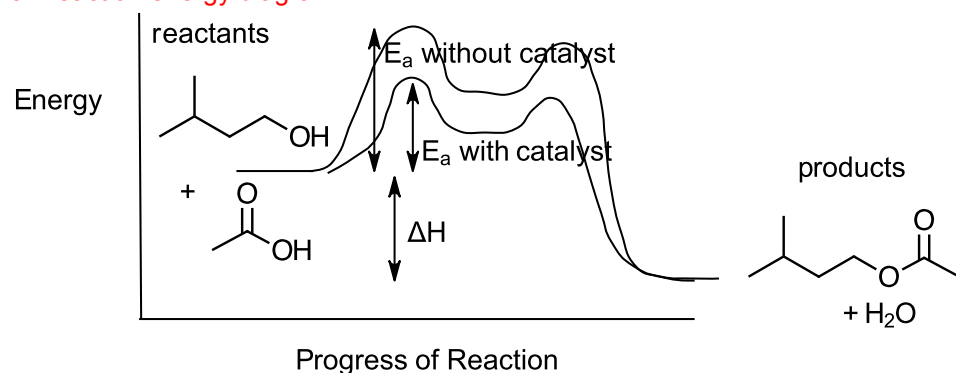
Rate constant changes with change in temperature.

Activation energy does not change with temperature or concentration but changes when a catalyst is used.

| Change in Reaction Condition | Reaction Rate | Rate Constant | Activation Energy |
|---------------------------------------|---------------|----------------|-------------------|
| Lower the temperature | decreases | decreases | stays the same |
| Use concentrated acetic acid solution | increases | stays the same | stays the same |
| Forget to add sulfuric acid | decreases | decreases | increases |

b. Sulfuric acid catalyst changes the reaction mechanism. A catalyst is involved in the mechanism (sequence in which bonds break and form) but not in the overall reaction.

c. Reaction energy diagram



This Reaction energy diagram shows a reaction mechanism with 2 elemental steps.

Reactants: isoamyl alcohol + acetic acid.

Products: isoamyl acetate + water.

Activation energy (E_a) is higher for the reaction without the H_2SO_4 catalyst so this reaction is slower.

Activation energy (E_a) is lower for the reaction with the H_2SO_4 catalyst so this reaction is faster.

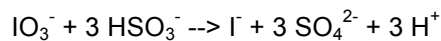
The saddle to the right of the 1st energy barrier (speed bump) represents the energy of the reaction intermediate – the product of the 1st elemental step of the reaction mechanism.

Note the 2nd energy barrier (speed bump) has a small activation energy and occurs fast. This means the reaction intermediate forms the product fast.

This also tells us the 1st elemental step is the slow or rate determining step of the reaction mechanism.

This reaction energy diagram shows ΔH is less than 0, which means this reaction is exothermic.

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



The rate law was determined by experiment to be: $\text{rate} = k [\text{IO}_3^-] [\text{HSO}_3^-]$

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.

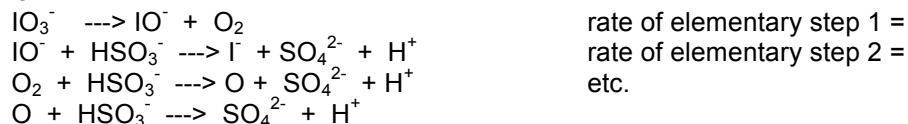
Here is a possible reaction mechanism for the iodine clock reaction and the rate law for each elementary step:



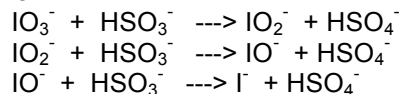
Compare the rate law for each elementary step to the experimental rate law ($\text{rate} = k [\text{IO}_3^-] [\text{HSO}_3^-]$). The rate law of the first elementary step matches the experimental rate law so this reaction mechanism is a possible mechanism for the iodine clock reaction. Since the rate 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 each elementary step.

Mechanism A:



Mechanism B:



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

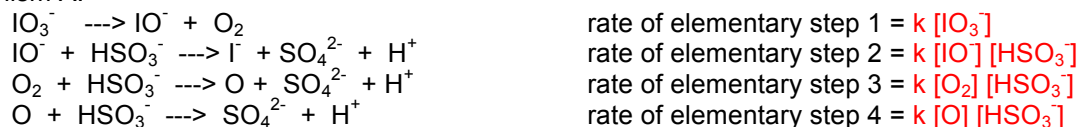
d. Which mechanism, A or B, is a possible mechanism for the iodine clock reaction? Give reasons.

Answers:

a. The slowest step in a reaction mechanism is called the **rate determining step**.

b and c.

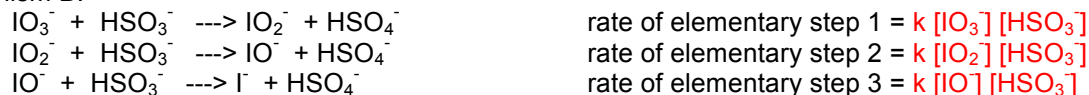
Mechanism A:



Overall: $\text{IO}_3^- + 3 \text{HSO}_3^- \rightarrow \text{I}^- + 3 \text{SO}_4^{2-} + 3 \text{H}^+$ This matches the iodine clock reaction.

None of the rate laws of the elemental steps matches the experimental rate law.

Mechanism B:



Overall: $\text{IO}_3^- + 3 \text{HSO}_3^- \rightarrow \text{I}^- + 3 \text{HSO}_4^{2-}$ This does not match the iodine clock reaction.

Elemental step 1 matches the experimental rate law.

d. Mechanism A: the sum of the elemental steps matches the iodine clock reaction but **NONE** of the rate laws of the elemental steps matches the experimental rate law ==> this not a possible mechanism.

Mechanism B: the sum of the elemental steps does **NOT** match the iodine clock reaction but Elemental step 1 matches the experimental rate law ==> this not a possible mechanism.

Note: When we study acid-base equilibrium reactions later this semester, we will learn HSO_4^{2-} is a weak acid that dissociates into $\text{SO}_4^{2-} + \text{H}^+$ ions under certain conditions.

If the iodine clock reaction is performed under these conditions, we can write this reaction

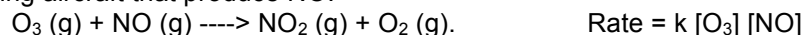


as



If iodine clock reaction is performed under these conditions, then Mechanism B is a possible mechanism.

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:



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) $O_3 \rightarrow O_2 + O$
 $O + NO \rightarrow NO_2$
- (ii) $O_3 + NO \rightarrow NO_3 + O$
 $NO_3 + O \rightarrow NO_2 + O_2$
- (iii) $NO \rightarrow N + O$
 $O + O_3 \rightarrow 2 O_2$
 $O_2 + N \rightarrow NO_2$
- (iv) $O_3 + NO \rightarrow NO_2 + O_2$

- 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?

Answers:

Mechanism

- (i) $O_3 \rightarrow O_2 + O$ rate = $k [O_3] \Rightarrow$ does not match experimental rate law.
 $O + NO \rightarrow NO_2$ rate = $k [O] [NO] \Rightarrow$ does not match experimental rate law.
Overall: $O_3 + NO \rightarrow O_2 + NO_2$

- (ii) $O_3 + NO \rightarrow NO_3 + O$ rate = $k [O_3] [NO] \Rightarrow$ matches experimental rate law.
 $NO_3 + O \rightarrow NO_2 + O_2$ rate = $k [NO_3] [O] \Rightarrow$ does not match experimental rate law.
Overall: $O_3 + NO \rightarrow O_2 + NO_2$

- (iii) $NO \rightarrow N + O$ rate = $k [NO] \Rightarrow$ does not match experimental rate law.
 $O + O_3 \rightarrow 2 O_2$ rate = $k [O] [O_3] \Rightarrow$ does not match experimental rate law.
 $O_2 + N \rightarrow NO_2$ rate = $k [O_2] [N] \Rightarrow$ does not match experimental rate law.
Overall: $O_3 + NO \rightarrow O_2 + NO_2$

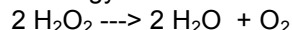
- (iv) $O_3 + NO \rightarrow NO_2 + O_2$ rate = $k [O_3] [NO] \Rightarrow$ matches experimental rate law.
Overall: $O_3 + NO \rightarrow NO_2 + O_2$

c. Mechanisms (ii) and (iv) are possible mechanisms. Each mechanism has an elemental step in which the rate law that matches the experimental rate law.

In Mechanisms (ii), the rate law of the 1st elemental step matches the experimental rate law so the 1st elemental step is the rate determining step.

In Mechanisms (iv), the rate law of the only elemental step matches the experimental rate law so the this elemental 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.

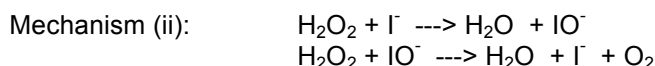
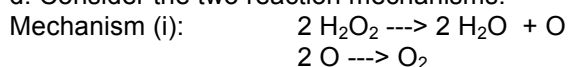


The rate law for the H_2O_2 decomposition without a catalyst is: rate = $k [H_2O_2]^2$

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:



- (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?

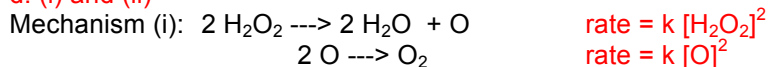
Answers:

a. H_2O_2 decomposition reaction is slow. We know because we do not see O_2 gas bubbles form when we look at H_2O_2 solution – this tells us H_2O_2 is not decomposing or is decomposing very slowly.

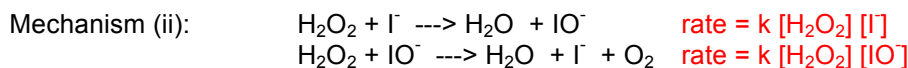
b. Activation energy does not change if temperature increases. Rate constant (k) changes if temperature increases.

c. The activation energy changes if a catalyst is used.

d. (i) and (ii)



Overall: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \Rightarrow$ this is the H_2O_2 decomposition reaction



Overall: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \Rightarrow$ this is the H_2O_2 decomposition reaction

(iii) Mechanism (ii) fits the catalyzed H_2O_2 decomposition because the I^- catalyst is involved in the reaction mechanism. The 1st elementary step is the rate determining step because it matches the experimental rate law.

(iv) For the catalyzed H_2O_2 decomposition mechanism, the 2nd elementary step regenerates the I^- catalyst.