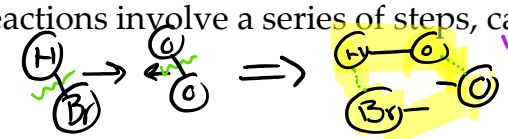
VIII) Reaction Mechanisms

Monday, September 11, 2017 2:27 PM

Reactions are expressed using a reaction equation. The equation gives information about the reactants and products, but very little information about the process that occurs to get from reactants to products. An equation suggests a one step process, which is in reality seldom the case. Most reactions involve a series of steps, called a **reaction mechanism.**



Example: $4HBr + O_2 \Rightarrow 2H_2O + 2Br_2$

The chemical reaction above actually has a three step mechanism. Why doesn't this reaction occur in one step (think about the collisions that would have to occur)?

Because the probability that 4 molecules of HBr and 1 O_2 will collide with correct collision geometry + sufficient energy is low ..... the rxn happens in steps.

The three step mechanism for HBr reacting with O_2:

Step 1: $HBr + O_2 \Rightarrow HOOBr + energy$ rate: fast exothermic ↓Ea

Step 2: $HOOBr + HBr + energy \Rightarrow 2HOBr$ rate: fast endothermic ↓Ea

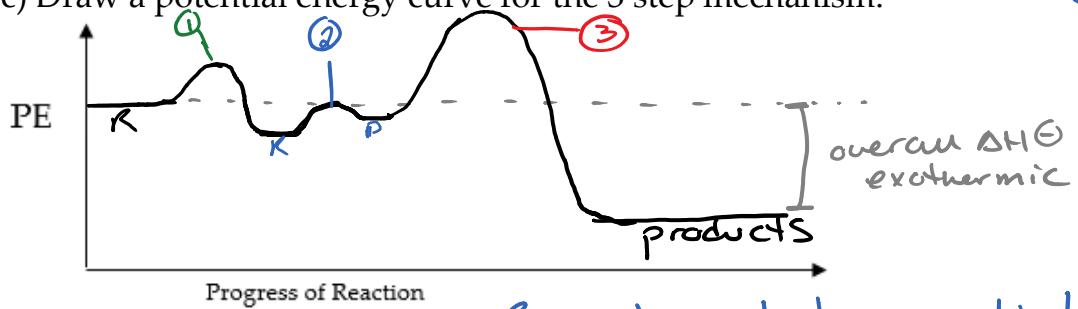
Step 3: $2HOBr + 2HBr \Rightarrow 2H_2O + 2Br_2 + energy$ rate: slow exothermic ↑Ea

Overall: $4HBr + O_2 \Rightarrow 2H_2O + 2Br_2 + energy$ ΔH = negative ✓ exothermic

a) Which step is the rate-determining step and why? Step 3: b/c it is the slowest.

b) Why are HOOBr and HOBr not part of the overall reaction equation? → b/c as soon as they are produced they are used in the next step.

c) Draw a potential energy curve for the 3 step mechanism.



HOOBr and HOBr are called Reaction Intermediates.

Define **Reaction Intermediate:** often produced in step 1 ... and subsequently used up in step 2. They "cancel out" in the overall rxn.

Notice that reaction intermediates are not part of the overall reaction because they "cancel out".

The first place you will see a reaction intermediate is on the product **side and then subsequently on the** reactant **side.** (*note a catalyst is the opp. show up as a R .... then a P ... unchange)

Example:

Step 1: $O_3 + NO + energy \Rightarrow NO_2 + O_2$ rate: fast ↓Ea endothermic

Step 2: $NO_2 + O \Rightarrow NO + O_2 + energy$ rate: slow ↑Ea exothermic

catalyst. rxn intermediate

a) What is the overall reaction? $O_3 + O \Rightarrow 2O_2$

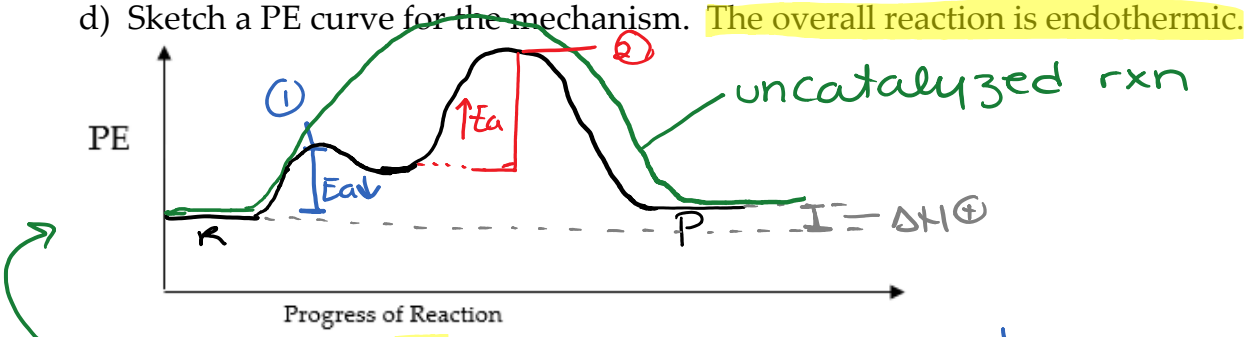
b) State any reaction intermediates. NO_2

a) What is the overall reaction? O_3 + ... + ... + O_2

b) State any reaction intermediates. NO_2

c) Which is the rate determining step? Step 2: slowest.

d) Sketch a PE curve for the mechanism. The overall reaction is endothermic.



What was the role of NO in the last example? catalyst

Catalyst: a substance that increases the rate without being consumed in a reaction

The involvement of NO created a different, lower energy mechanism for the reaction.

What happened with NO in step 1? collides with O_3 to produce NO_2 . it was consumed

What happened with NO in step 2? collides with "O" to produce O_2 and regenerate the catalyst "NO"

Why must catalyzed reactions involve a two-step mechanism?

To allow the catalyst to regenerate.

A catalyst is usually not part of the overall reaction (not a reactant or product) because it "cancels out".

You'll see a catalyst on the Reactant **side first, and then on the** product. **side.**

Example: (catalyst ↓; don't show up in "overall rxn" ∴ they must show up as reactants in order to "cancel out")

Step 1: $Br_2 + H_2O_2 \Rightarrow 2Br^- + 2H^+ + O_2$ ("cancel out")

Step 2: $2Br^- + 2H^+ + H_2O_2 \Rightarrow Br_2 + 2H_2O$ (rxn intermediates)

Overall: $2H_2O_2 \Rightarrow 2H_2O + O_2$

a) Determine step 2. (see above)

b) Identify any reaction intermediates. Br^- and H^+ b/c they are produced in step 1, and subsequently used up.

c) Identify any catalysts. Br_2 b/c it shows up first as a reactant, then as a product in the end, unchanged.

Assignment 6: Reaction Mechanism Exercises

1) Step 1: $2NO + H_2 \Rightarrow N_2 + H_2O_2$ rate: slow

Step 2: $H_2O_2 + H_2 \Rightarrow 2H_2O$ rate: fast

a) What is the overall reaction?

b) Which is the rate determining step?
c) Identify any reaction intermediates.

2) Step 1: rate: fast

Step 2: $\underline{N_2O_2 + Br_2 \Rightarrow 2NOBr}$ rate: slow

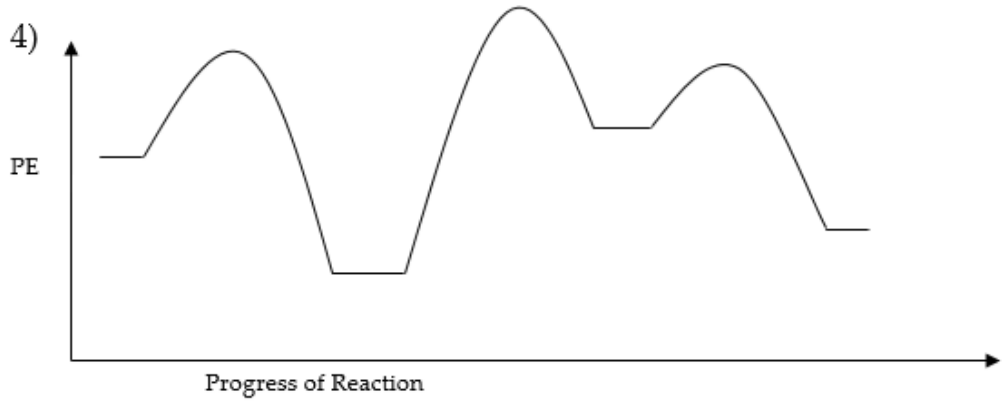
Overall: $2NO + Br_2 \Rightarrow 2NOBr$

a) Find Step 1.
b) If it was possible to increase the rate of step 1, how would this affect the overall reaction rate?
c) Identify any reaction intermediates.

3) Why does the following reaction have a multi-step mechanism?

$3FeCl_2 + KNO_3 + 4HCl \Rightarrow 3FeCl_3 + NO + 2H_2O + KCl$

4)



a) How many steps make up the reaction mechanism?
b) State whether each step is endothermic or exothermic.
c) Is the overall reaction endothermic or exothermic?
d) Which is the rate determining step? How can you tell?
e) Label ΔH for the overall reaction on the curve.
f) On the curve, label an A wherever there is an activated complex and an I wherever there is a reaction intermediate. How do the two differ?

5) Consider the following mechanism:

Step 1: $NO_2 + Mn \Rightarrow NO_2Mn$

Step 2:

Step 3: $\underline{NO_3 + CO \Rightarrow NO_2 + CO_2}$

Overall: $NO_2 + CO \Rightarrow NO + CO_2$

a) Determine Step 2.
b) Identify a catalyst.
c) Identify any reaction intermediates.
d) What would be the chemical formula of the activated complex in Step 3?

6) Step 1: $H^+ + H_2O_2 \Rightarrow H_3O_2^+$ rate: fast

Step 2: rate: slow

Overall: $H^+ + I^- + H_2O_2 \Rightarrow H_2O + HOI$

a) Detemine Step 2.
b) Identify any reaction intermediates.
c) Which is the rate determining step?

d) What is the formula for the activated complex in Step 2?
(don't forget to sum charges!)

7) Step 1: $ClO^- + ClO^- \Rightarrow ClO_2^- + Cl^-$
Step 2: $ClO_2^- + ClO^- \Rightarrow ClO_3^- + Cl^-$

a) What is the overall reaction?

b) What would the chemical formula be for the activated complex in Step 1? (don't forget to sum charges!)

c) Identify any reaction intermediates.

8) Step 1: $NO + NO \Rightarrow N_2O_2$ exothermic / rate: fast
Step 2: endothermic / rate: slow
Step 3: $N_2O_4 \Rightarrow 2NO_2$ exothermic / rate: fast
Overall: $2NO + O_2 \Rightarrow 2NO_2$ exothermic

a) Determine Step 2.

b) Sketch a PE diagram for the reaction mechanism.