MECHANISMS

Mechanism: how reactants are converted to products at the molecular level.

The sequence of events that describes the actual process by which reactants become products is called the reaction mechanism.

Reactions may occur all at once or through several discrete steps.

Each of these processes is known as an elementary reaction or elementary process.

Mechanisms

O_3 + NO reaction occurs in a single ELEMENTARY step. Most others involve a sequence of elementary steps.

An elementary step= one whose rate law can be written from its molecularity.

Molecularity = the number of species that must collide to produce the reaction indicated for that step.

Adding elementary steps gives NET reaction.

Molecularity	Elementary Reaction	Rate Law
*Uni*molecular	$A \longrightarrow$ products	Rate = $k[A]$
*Bi*molecular	$A + A \longrightarrow$ products	Rate = $k[A]^2$
*Bi*molecular	$A + B \longrightarrow$ products	Rate = $k[A][B]$
*Ter*molecular	$A + A + A \longrightarrow$ products	Rate = $k[A]^3$
*Ter*molecular	$A + A + B \longrightarrow$ products	Rate = $k[A]^2[B]$
*Ter*molecular	$A + B + C \longrightarrow$ products	Rate = $k[A][B][C]$

Mechanisms

Most reactions involve a sequence of elementary steps that must satisfy two requirements…

$$2\,I^- + H_2O_2 + 2\,H^+ \text{ ---> } I_2 + 2\,H_2O$$

$$\text{Rate} = -k\,[I^-]\,[H_2O_2]$$

REQUIREMENTS

1. **The sum of the elementary steps must give the overall balanced equation for the reaction.**
2. **The mechanism must agree with the experimentally determined rate law.**

Mechanisms

Most reactions involve a sequence of elementary steps.
$2\ I^- + H_2O_2 + 2\ H^+ \text{ ---> } I_2 + 2\ H_2O$
Rate = $-k\ [I^-]\ [H_2O_2]$

Proposed Mechanism

Step 1 — slow $H_2O_2 + I^- \text{ --> } H_2O + OI^-$

Step 2 — fast $H^+ + OI^- \text{ --> } HOI$

Step 3 — fast $HOI + H^+ + I^- \text{ --> } I_2 + H_2O$

- **Show that all three elementary steps add up to give the overall, stoichiometric equation. This will satisfy the first requirement.**

Solving a Problem

- **Step 1 — slow** $H_2O_2 + I^- \text{ --> } H_2O + \cancel{OI^-}$
- **Step 2 — fast** $H^+ + \cancel{OI^-} \text{ --> } \cancel{HOI}$
- **Step 3 — fast** $\cancel{HOI} + H^+ + I^- \text{ --> } I_2 + H_2O$

$$H_2O_2 + 2\ H^+ + 2\ I^- \rightarrow I_2 + 2\ H_2O$$

- **What is the molecularity of each step?**
  - **Step 1 and 2 are bimolecular, step 3 is termolecular**
- **For this mechanism to be consistent with kinetic data, what must be the experimental rate law?**

Mechanisms

Rate = $-k\ [I^-]\ [H_2O_2]$

$2\ I^- + H_2O_2 + 2\ H^+ \text{ ---> } I_2 + 2\ H_2O$
Step 1 — slow $H_2O_2 + I^- \text{ --> } H_2O + OI^-$
Step 2 — fast $H^+ + OI^- \text{ --> } HOI$
Step 3 — fast $HOI + H^+ + I^- \text{ --> } I_2 + H_2O$

Rate of the reaction controlled by slowest step —
RATE DETERMINING STEP= slowest step.
Rate can be no faster than rate determining step!

Elementary Step 1 is bimolecular and involves I^- and H_2O_2. Therefore, this predicts the rate law should be

Rate = $-k\ [I^-]\ [H_2O_2]$ — as observed!! This satisfies the second requirement.

The species HOI and OI^- are reaction intermediates.

Slow Initial Step

$NO_2\ (g) + CO\ (g) \longrightarrow NO\ (g) + CO_2\ (g)$

- The rate law for this reaction is found experimentally to be $\text{Rate} = k\,[NO_2]^2$
- CO is necessary for this reaction to occur, but the *rate* of the reaction does not depend on its concentration.
- This suggests the reaction occurs in two steps.
- A proposed mechanism for this reaction is

  Step 1: $NO_2 + NO_2 \longrightarrow NO_3 + NO$ (slow)

  Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$ (fast)
- The NO_3 intermediate is consumed in the second step.
- As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.

Fast Initial Step

$2\ NO\ (g) + Br_2\ (g) \longrightarrow 2\ NOBr\ (g)$

- The rate law for this reaction is found to be

  $$\text{Rate} = k\,[NO]^2\,[Br_2]$$
- Because termolecular processes are rare, this rate law suggests a two-step mechanism.
  - A proposed mechanism is

    Step 1: $NO + Br_2 \longleftrightarrow NOBr_2$ (fast)

    Step 2: $NOBr_2 + NO \longrightarrow 2\ NOBr$ (slow)

Step 1 includes the forward *and* reverse reactions.

Fast Initial Step

- The rate of the overall reaction depends upon the rate of the slow step.
- The rate law for that step would be

  $$\text{Rate} = k_2\,[NOBr_2]\,[NO]$$
- But how can we find $[NOBr_2]$?
- $NOBr_2$ can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br_2
- The reactants and products of the first step are in equilibrium with each other.
- Therefore, $\text{Rate}_f = \text{Rate}_r$

- Because $Rate_f = Rate_r$,

$$k_1 [NO] [Br_2] = k_{-1} [NOBr_2]$$

- Solving for $[NOBr_2]$ gives us

$$\frac{k_1}{k_{-1}} [NO] [Br_2] = [NOBr_2]$$

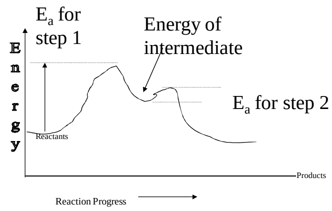
Substituting this expression for $[NOBr_2]$ in the rate law for the rate-determining step gives

(Rate = k_2 $[NOBr_2]$ [NO])

$$\text{Rate} = \frac{k_2 k_1}{k_{-1}} [NO] [Br_2] [NO]$$

$$= k [NO]^2 [Br_2]$$ AHA!!

Reaction Mechanism Graph



This is a two-step reaction mechanism, involving one intermediate. The reaction is slightly exothermic. And step 1 is the rate-determining step!

Lab Calculations for "R"

- Use the formula $M_1V_1 = M_2V_2$ to calculate all concentrations, where
- M_1 = original molarity
- V_1 = volume added
- M_2 = unknown
- V_2 = final total volume

My table of results

concentration	1	2	3	4	5	6	7
KI = $[I^-]$							
$[S_2O_3^{2-}]$							
$[S_2O_8^{2-}]$							
$[I_2]$							
Average Time							
$[I_2]$ /time							

In regards to the graphs…

- You may have to plot [A] vs. time, Ln [A] versus time, or 1/[A] versus time to find the straight line and the reaction order.
- Do you need graph paper???