**5.111 Lecture Summary #32** **Monday, December 1, 2014**

**Reading for Today**: 14.7-14.8, 14.10 in $5^{th}$ ed and 13.7-13.8, 13.10 in $4^{th}$ ed
**Reading for Lecture #33**: 14.11-14.13 in $5^{th}$ ed and 13.11-13.13 in $4^{th}$ ed

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**Topic: Kinetics**
I. Investigating Reaction Mechanisms

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**I. Investigating Reaction Mechanisms.** To describe how a reaction takes place, we propose a reaction mechanism, which is the series of steps (or _________________________) that take place to convert reactants to products. We then examine whether the mechanism is consistent with experimental data. Since the mechanism can affect the overall rate of the reaction, it is important to understand which steps are slow and which are fast.

**<u>Example 1</u>**: $2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$

It is experimentally determined that the rate of formation of $NO_2$ is $k_{obs}\ [NO]^2[O_2]$

Overall order = ________ Is a one step mechanism likely? _______

____ molecular reactions are rare

Proposed mechanism

Step 1 $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

forward rate =

order= ____molecular

reverse rate =

order= ____molecular

Step 2 $O_2 + N_2O_2 \xrightarrow{k_2} NO_2 + NO_2$

rate =

order= ____molecular

What is the rate of $NO_2$ formation? $NO_2$ is formed in step 2 and the rate equals:

rate of formation of $NO_2 = 2k_2\ [O_2][N_2O_2]$

(The factor of 2 appears because two molecules of $NO_2$ are formed; so the concentration of $NO_2$ increases twice as fast as the concentration of $N_2O_2$ decreases).

but this rate law includes an intermediate, $[N_2O_2]$, and intermediates **<u>must not</u>** appear in a final rate law. We must solve for $[N_2O_2]$ in terms of reactants, products, and rate constants.

net rate of formation of $N_2O_2$ =

At this point, we use the steady-state approximation.

**Steady-state approximation**: the rate of formation of intermediates _______________ rate of decay of intermediates.

Net rate = _______ = $k_1 [NO]^2 - k_{-1} [N_2O_2] - k_2 [N_2O_2][O_2]$

Solving for $[N_2O_2]$:

Substituting into rate of formation of $NO_2 = 2k_2 [O_2][N_2O_2]$

$$\text{rate of formation of } NO_2 = \frac{2 k_1 k_2 [O_2] [NO]^2}{k_{-1} + k_2 [O_2]}$$

This would be the answer if the mechanism had no fast or slow steps. The above rate law is inconsistent with the experimentally determined rate law ($k_{obs} [NO]^2[O_2]$), so the mechanism must have ___________________________________ steps.

What if the first step is fast and reversible, and the second step is slow?

Step 1 (__________ ________________) $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

Step 2 ( ________) $O_2 + N_2O_2 \xrightarrow{k_2} NO_2 + NO_2$

The slowest elementary step in a sequence of reactions is called the **rate determining step (RDS)**.

A rate determining step is so much slower than the rest of the steps that it ____________ the rate of the overall reaction.

Given this proposal about fast and slow steps, we can simplify based on the consideration that the decomposition of $N_2O_2$ is faster than the consumption of $N_2O_2$.

| | | |
|---|---|---|
| $k_{-1} [N_2O_2]$ | >>> | $k_2 [N_2O_2][O_2]$ |
| rate of decomposition of $[N_2O_2]$ | is faster than | rate of consumption |

with $k_{-1} >> k_2 [O_2]$ and the term "$k_2 [O_2]$" drops out

$$[N_2O_2] = \frac{k_1 [NO]^2}{k_{-1} + \cancel{k_2 [O_2]}} \qquad \text{(original expression)}$$

Leaving:

$$[N_2O_2] = \frac{k_1}{k_{-1}} [NO]^2 \quad \text{or} \quad \frac{[N_2O_2]}{[NO]^2} = \frac{k_1}{k_{-1}} = \qquad \text{equilibrium expression for the 1}^{\text{st}} \text{ step}$$

When a reversible fast step is followed by a slow step, the first step approaches **equilibrium**. Not much of the product is being siphoned off by the second step, so an equilibrium-like condition is reached.

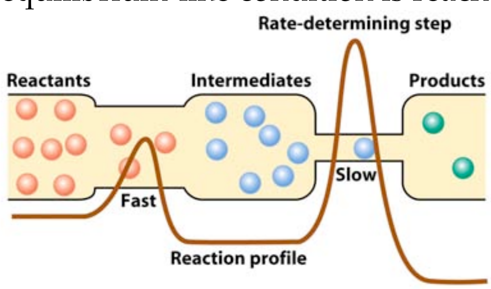


Figure by MIT OpenCourseWare.

Now we can substitute $\frac{k_1}{k_{-1}} [NO]^2$ or $K_1 [NO]^2$ for $[N_2O_2]$

$$\text{rate} = 2k_2 [O_2][N_2O_2] = \frac{2k_1k_2 [O_2][NO]^2}{k_{-1}} \quad \text{or} \quad 2K_1k_2 [O_2][NO]^2$$

$k_{obs} = 2K_1k_2$ $\quad$ $\underline{k_{obs} \text{ is the } \textbf{observed} \text{ rate constant}}$

$\text{rate} = k_{obs} [O_2][NO]^2$ $\quad$ agrees with experimental data (first step must be fast and reversible, and that must be followed by a slow step)

**Example 2**: The following mechanism has been proposed for $2NO + Br_2 \rightarrow 2NOBr$
If the experimental rate law is $k_{obs}$ $[NO][Br_2]$, determine which step is slow.

1st $\quad NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2 \qquad$ $rate_f$=

$rate_r$=

2nd $\quad NOBr_2 + NO \xrightarrow{k_2} 2NOBr \qquad$ rate=

rate of formation of NOBr = $2k_2 [NOBr_2][NO]$ $\qquad$ but $[NOBr_2]$ is an intermediate

Solve for intermediate in terms of rate constants, reactants and/or products:

change in $[NOBr_2]$ =

Steady state approximation: $\quad 0 = k_1 [NO][Br_2] - k_{-1} [NOBr_2] - k_2 [NOBr_2][NO]$

Rearranging:

$k_{-1} [NOBr_2] + k_2 [NOBr_2][NO] = k_1 [NO][Br_2]$

$[NOBr_2] (k_{-1} + k_2 [NO]) = k_1 [NO][Br_2]$

$$[NOBr_2] = \frac{k_1 [NO][Br_2]}{k_{-1} + k_2 [NO]}$$

Substitute back into $2k_2 [NOBr_2][NO]$ to get:

$$\text{rate of formation of NOBr} = \frac{2k_1 k_2 [NO]^2 [Br_2]}{k_{-1} + k_2 [NO]}$$

If first step is slow
and second step is fast $\qquad k_2[NO] >> k_{-1}$ $\qquad$ rate =

rate =

overall order =

If first step is fast
and second step is slow $\qquad k_{-1} >> k_2[NO]$ $\qquad$ rate =

rate =

overall order =

The experimental rate law $k_{obs}$ $[NO][Br_2]$ is consistent with a slow first step and a fast second step.

**Example 3**: Write the rate law for $2O_3 \rightarrow 3O_2$ given that the first step is fast and reversible, and the second step is slow.

| | | |
|---|---|---|
| Step 1 (fast reversible) | $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ | $rate_f =$ <br> $rate_r =$ |
| Step 2 (slow) | $O + O_3 \xrightarrow{k_2} O_2 + O_2$ | rate= |

The rate is determined by the slowest step

The rate of formation of $O_2$ is equal to 2 times the rate of the slow step ($k_2[O][O_3]$), since two molecules of $O_2$ are formed.

Thus, rate of formation of $O_2 = 2k_2[O][O_3]$, but "O" is an intermediate, solve for "O" in terms of products and reactants and rate constants.

Since the first step is fast and reversible and the second step is slow, the first step is in equilibrium and we can write

$$\frac{[O_2][O]}{[O_3]} = \frac{k_1}{k_{-1}} = K_1 \qquad \text{or} \qquad [O] = \frac{k_1 [O_3]}{k_{-1} [O_2]}$$

Substituting:

$$\text{rate} = \frac{2k_2 k_1 [O_3]^2}{k_{-1} [O_2]}$$

$$\text{rate} = k_{obs} \frac{[O_3]^2}{[O_2]}$$

What is the order in $O_3$? double $O_3$/rate will?

What is the order in $O_2$? double $O_2$/

What is the overall order? double both $O_3$ and $O_2$/