5.111 Lecture 33

Kinetics Topics: Reaction Mechanisms Chapter 13 p 549-552 (p 502-505 in 3rd ed)

Investigating Reaction Mechanisms (Ch 13.8)

$2NO (g) + O_2 (g) \rightarrow 2NO_2 (g)$

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?

Proposed mechanism

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

order= molecularity=

reverse rate =

order= molecularity=

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

order= molecularity=

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 expression includes an intermediate, $[N_2O_2]$, and is therefore not acceptable.

Solve for $[N_2O_2]$ in terms of reactants, products, and rate constants:

net rate of formation of $N_2O_2 = k_1 [NO]^2 - k_{-1} [N_2O_2] - k_2 [N_2O_2][O_2]$

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

Steady-state approximation ≡ net rate of formation of an intermediate equals zero or rate of formation of an intermediate equals the rate of disappearance of an intermediate.

Net rate = 0 = $k_1\ [NO]^2 - k_{-1}\ [N_2O_2]\ -\ k_2\ [N_2O_2][O_2]$

solving for $[N_2O_2]$:

rearranging:

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

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

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, so the mechanism must have fast and slow steps.

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

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

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

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 governs the rate of the overall reaction.

Given this proposal about fast and slow steps, we can simply our expression for the intermediate

$$[N_2O_2] \quad = \quad \frac{k_1\,[NO]^2}{k_{-1} + k_2\,[O_2]}$$

by considering that the decomposition of N_2O_2 is faster than the consumption of N_2O_2. Therefore:

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

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

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

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

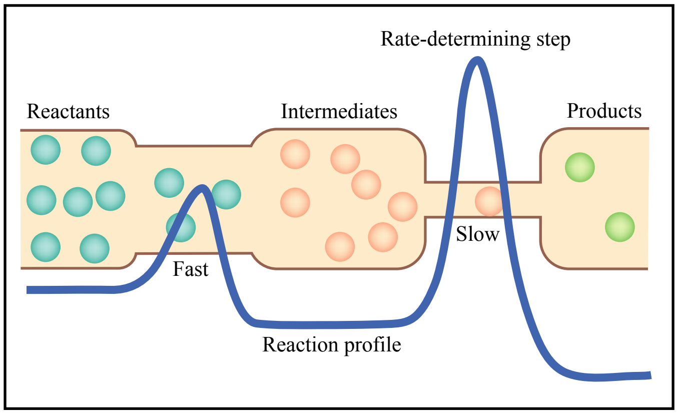

Figure by MIT OpenCourseWare.

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

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

$k_{obs} = 2K_1k_2$ observed rate constant ≡ k_{obs}

$\text{rate} = k_{obs}\,[O_2][NO]^2$ agrees with experimental data

Another example $2O_3 \rightarrow 3O_2$

proposed mechanism:

Step 1 (fast reversible) $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ rate_f=

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/

Another Example

If you know the experimental rate law (rate = k_{obs} [NO][Br_2]), you can determine which step is slow.

Proposed mechanism for $2NO + Br_2 \rightarrow 2NOBr$

1st $NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2$ rate$_f$=

rate$_r$=

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

rate of formation of NOBr = $2k_2 [NOBr_2][NO]$

but [$NOBr_2$] is an intermediate

change in [$NOBr_2$] =

steady state approximation:

$$0 = k_1 [NO][Br_2] - k_{-1} [NOBr_2] - k_2 [NOBr_2][NO]$$

rearranging:

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

Substituting:

$$\text{rate of formation of NOBr} = \frac{2k_1k_2 [NO]^2 [Br_2]}{k_{-1} + k_2 [NO]}$$

If first step is slow $k_2[NO] \gg k_{-1}$ rate =

and second step is fast rate = overall order =

If first step is fast $k_{-1} \gg k_2[NO]$ rate =

and second step is slow

rate = overall order =

The experimental rate law is consistent with a slow first step and a fast second step.

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