

Reaction Mechanisms

- ✗ A reaction mechanism is step or series of steps that make up a reaction.
- ✗ The steps in a reaction mechanism are referred to as **elementary steps**.
- ✗ **Molecularity** refers to the number of reactant molecules involved in an elementary step.

Unimolecular:

Bimolecular:

Termolecular:

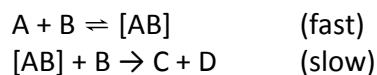
- ✗ Lower molecular steps tend to be faster than ones with more molecules.
- ✗ The rate determining step is the slowest step in the reaction mechanism and will have the largest activation energy.

Using Reaction Mechanisms to Determine the Rate Law Equation

- ✗ The rate law expression can be determined from the reaction mechanism.
- ✗ The rate determining step is the elementary step that determines the rate law expression.
- ✗ The rate of a reaction is proportional to the concentrations of the reactants in the rate determining step raised to their molar coefficients.
- ✗ If any reaction intermediates appear in this expression, you must use the other steps to eliminate these species.

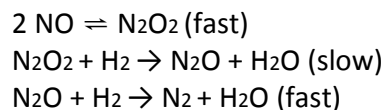
Example 1

The reaction, $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$ occurs by the mechanism below. Use that mechanism to determine the rate law expression.



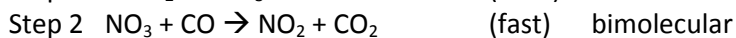
Example 2

The reaction between NO and H₂ is believed to occur in the following three-step process. Write the overall equation for this reaction and the rate law expression.



Worksheet

1. The reaction between nitrogen dioxide and carbon monoxide occurs in the 2 step process below.



- a) State the molecularity of each step.
b) Write the equation for the overall reaction and identify and reaction intermediates.

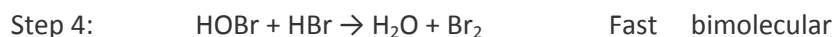
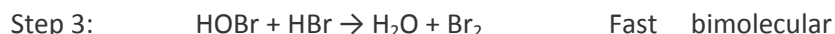
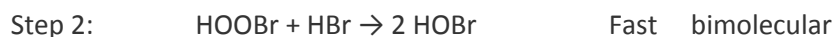
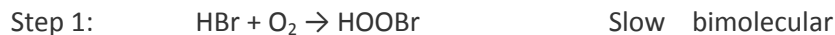


- c) Write the rate law expression.

Use Step 1 as it is the rate determining step

$$r = k[\text{NO}_2]^2$$

2. The reaction between hydrogen bromide and oxygen gas, occurs in the 4 step process below.



- a) State the molecularity of each step.
b) Write the equation for the overall reaction and identify and reaction intermediates.

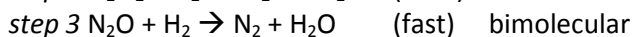
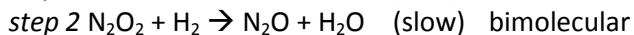


- c) Write the rate law expression.

Use Step 1 as it is the rate determining step

$$R = k[\text{HBr}][\text{O}_2]$$

3. Given the following mechanism:



- a) State the molecularity of each step.
b) Write the equation for the overall reaction and identify and reaction intermediates.



- c) Write the rate law expression.

Use Step 2 as it is the Rate determining step

$$r = k[\text{N}_2\text{O}_2][\text{H}_2]$$

** N_2O_2 is a reaction intermediate so it must be replaced using step 1

$[\text{N}_2\text{O}_2]$ can be replaced by $[\text{NO}]^2$ since step 1 is a reversible reaction

$$r = k[\text{NO}]^2[\text{H}_2]$$

4. The kinetics of the reaction: $2X + Y \rightarrow Z$ was studied and the results are:

Trial	[X]	[Y]	Rate (mol/Ls)
1	0.20	0.10	7.00×10^{-4}
2	0.20	0.20	1.40×10^{-3}
3	0.40	0.20	1.40×10^{-3}

a) Use the data above to determine the rate law equation, including the value of k with correct units.

For X, compare 2 and 3 [X] x 2 rate x 1 therefore zero order in X

For Y, compare 1 and 2 [Y] x 2 rate x 2 therefore first order in Y

$$r = k[Y]$$

to find k sub in trial 1

$$7.00 \times 10^{-4} = k(0.10)$$

$$k = 7.00 \times 10^{-3}$$

$$r = 7.00 \times 10^{-3}[Y]$$

Below are 3 proposed mechanisms for this reaction.

b) What is the overall reaction for each mechanism?

c) What is the molecularity of each step?

d) What is the rate law derived from each mechanism?

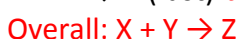
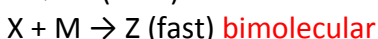
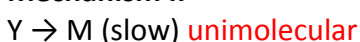
e) Which mechanism is consistent with the rate law from part a?

Mechanism I



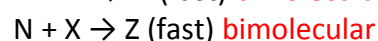
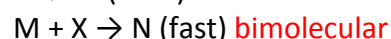
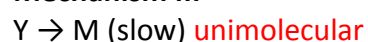
$$r = k[X][Y]$$

Mechanism II



$$r = k[Y]$$

Mechanism III



$$r = k[Y]$$

Mechanism III is consistent with the rate law from part a