



Kinetics Unit Activity – Kinetic Mechanisms KEY

The rate of a chemical reaction and specifically how that rate depends on concentration are determined by the “mechanism” of the reaction. The mechanism is a chemist’s microscopic view of how the reaction is actually happening. A mechanism consists of a number of **elementary steps** that are the individual chemical transformations that make up the overall reaction. The rate of the overall reaction is determined by the rates of the elementary steps. The most important step is the slowest step that is called the **rate limiting step**.

Elementary steps in chemical reactions can be broadly broken down into two types of reactions.

Unimolecular. These are steps in which a single molecule does something (typically breaks a bond). The key is that these steps involve only a single reactant species.

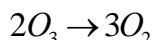
Bimolecular. These steps involve two reactant molecules: two molecules that collide and then react.

Whereas, rate laws CANNOT be deduced from the overall reaction, the individual rate laws for elementary steps CAN be deduced from the elementary reactions!

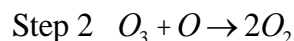
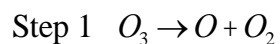
Unimolecular steps are first-order

Bimolecular steps are overall second-order

Consider the following overall reaction that is the decomposition of ozone



How does this reaction actually take place? Do two ozone molecules collide and rearrange into three oxygen molecules? Or does something else happen? Kinetics studies show that the reaction actually follows this two-step mechanism



1. Write out in words a description of each elementary step in the mechanism

Step 1 - The decomposition of an ozone molecule (O_3) into a single oxygen atom (O) and an oxygen gas molecule (O_2). One species breaks into two.

Step 2 - The synthesis of two oxygen gas molecules ($2O_2$) from a single oxygen atom (O) and an ozone molecule (O_3). Two species collide.

2. State whether each step is unimolecular, bimolecular, or something else.

Step 1 - Unimolecular. There is only one substance on the reactant side.



Step 2 - Bimolecular. There are two different substances on the reactant side.

3. Write the expected rate law for each step. (note: each step will have a different rate constant. So denote the rate constant for the first step as k_1 and the second as k_2)

Step 1: $\text{Rate}_1 = k_1[\text{O}_3]$ (Rate laws for unimolecular are first order).

Step 2: $\text{Rate}_2 = k_2[\text{O}_3][\text{O}]$ (Rate laws for bimolecular are second order).

Reaction mechanisms often have **intermediates**. Intermediates are chemical species that appear during the reaction but are not part of the overall reaction.

4. Does the mechanism for the decomposition of ozone show any intermediate species? If so, what are they?

Yes, the single oxygen molecule (O) does not show up in the overall reaction, but appears in both steps as either a product or reactant.

The reason we cannot determine the rate law for an overall reaction from a balanced equation is that we don't know which steps are determining the rate. The important step in a chemical mechanism is the slowest step (and the steps that occur before it). This slow step is referred to as the **RATE LIMITING STEP** or the **RATE DETERMINING STEP**.

For the ozone reaction we can imagine two possibilities, either the first step is the slowest step or the second step is the slowest.

Mechanism #1		Mechanism #2		
Step 1	$\text{O}_3 \rightarrow \text{O} + \text{O}_2$	slow	Step 1 $\text{O}_3 \leftrightarrow \text{O} + \text{O}_2$	fast
Step 2	$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$	fast	Step 2 $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$	slow

5. What is the rate-limiting step in each reaction?

In mechanism 1, the rate-limiting step is step 1.

In mechanism 2, the rate-limiting step is step 2.

6. What is the rate law for the rate-limiting step in each reaction?

In mechanism 1: $\text{Rate}_1 = k_1[\text{O}_3]$

In mechanism 2: $\text{Rate}_2 = k_2[\text{O}_3][\text{O}]$

7. Do either of the rate laws contain any intermediates?

Yes, the rate law from mechanism 2 contains the single O molecule, which is an intermediate.

8. The first step in Mechanism #2 is an equilibrium. What is the rate law for the forward reaction? What is the rate law for the backward reaction? (note: the forward and backward



rate constants will be different. Denote the rate constant for the forward reaction as k_1 and the backward as k_{-1})

$$\text{Forward: Rate}_1 = k_1[\text{O}_3]$$

$$\text{Backward: Rate}_{-1} = k_{-1}[\text{O}][\text{O}_2]$$

9. What is the equilibrium constant for this reaction (write in terms of concentrations?)

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]}$$

10. Given that for equilibrium the forward rate and the backward rate must be equal, please write an expression for the **Equilibrium Constant** in terms of the **rate constants** for the forward and backward reactions?

$$\text{Forward: Rate}_1 = k_1[\text{O}_3]$$

$$\text{Backward: Rate}_{-1} = k_{-1}[\text{O}][\text{O}_2]$$

$$\text{Forward Rate} = \text{Backward Rate}$$

$$\text{Rate}_1 = \text{Rate}_{-1} = k_1[\text{O}_3] = k_{-1}[\text{O}][\text{O}_2]$$

Rearrange to look like the right-side of the equilibrium constant expression:

$$\frac{k_1}{k_{-1}} = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]}$$

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]}$$

$$\text{Therefore } K = \frac{k_1}{k_{-1}}$$

11. Can you use the equilibrium constant to eliminate the intermediate from the rate law for the rate-limiting step in Mechanism #2?

The rate-limiting step in mechanism 2 has a rate written like this: $\text{Rate}_2 = k_2[\text{O}_3][\text{O}]$

However, O is an intermediate in the overall reaction. We can rearrange the equilibrium constant, K, to solve for O using O_2 and O_3 .

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]}$$

$$[\text{O}] = \frac{K[\text{O}_3]}{[\text{O}_2]}$$

Plug this into the rate law:

$$\text{Rate}_2 = k_2[\text{O}_3]\left(\frac{K[\text{O}_3]}{[\text{O}_2]}\right)$$



We can combine k_2 and K into a single constant, just k :

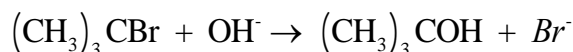
$$\text{Rate}_2 = \frac{k[\text{O}_3]^2}{[\text{O}_2]}$$

$$\text{Rate}_2 = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

12. Can you suggest an experiment to distinguish between these two mechanisms?

Design an experiment where the concentration of O_3 varies across two different experiments. Run an experiment with a particular concentration of O_3 and measure its initial rate. Then, run a second experiment with a doubled concentration of O_3 – if the rate also doubles then the reaction must be first-order with respect to O_3 , but if the rate quadruples then the reaction must be second-order with respect to O_3 . The first order conditions would match the rate law from proposed mechanism 1 and the second-order conditions would match the rate law from proposed mechanism 2.

NOW, let's look at a reaction that we have seen before:

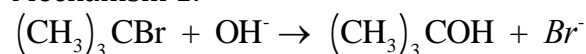


We will imagine two possible mechanisms by which this reaction can occur.

The first is a single step bimolecular reaction. The $(\text{CH}_3)_3\text{CBr}$ collides with the OH^- and reacts. In this case there is only one elementary step and it is the same as the overall reaction.

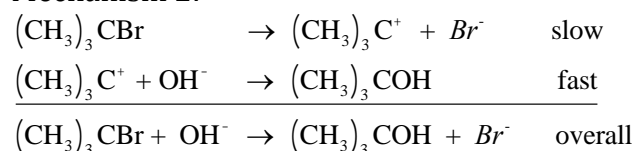
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Mechanism 1:



Another way this reaction might proceed is that first the $(\text{CH}_3)_3\text{CBr}$ might fall apart into $(\text{CH}_3)_3\text{C}^+$ and Br^- . Then the $(\text{CH}_3)_3\text{C}^+$ collides with an OH^- and reacts. We can write this down as

Mechanism 2:



Answer the following for each mechanism.



13. How many elementary steps does each mechanism have?

Mechanism 1 - One elementary step

Mechanism 2 - Two elementary steps.

14. Are there any intermediates in the mechanism?

Yes. In mechanism 2, $(\text{CH}_3)_3\text{C}^+$ is an intermediate.

15. Write the rate law you would expect for each step in the mechanism?

Mechanism 1 - $\text{Rate}_1 = k_1[(\text{CH}_3)_3\text{CBr}][\text{OH}^-]$

Mechanism 2 - Step 1 is $\text{Rate}_1 = k_1[(\text{CH}_3)_3\text{CBr}]$

Step 2 is $\text{Rate}_2 = k_2[(\text{CH}_3)_3\text{C}^+][\text{OH}^-]$

16. Which step in the mechanism is the **rate-determining step**?

Mechanism 1 - The first and only step must be the rate-determining step

Mechanism 2 - The first step (unimolecular).

17. What would you predict for an overall rate law for each mechanism?

Mechanism 1: $\text{Rate}_1 = k_1[(\text{CH}_3)_3\text{CBr}][\text{OH}^-]$

Mechanism 2: $\text{Rate}_2 = k_2[(\text{CH}_3)_3\text{CBr}]$

18. Given the data below can you decide which is the best mechanism for this reaction?

Experiment number	Initial $[(\text{CH}_3)_3\text{CBr}]$	Initial $[\text{OH}^-]$	Initial Rate M s^{-1}
1	1 M	1 M	0.025
2	2 M	1 M	0.050
3	1 M	2 M	0.025

Mechanism 2, because there is no dependence on the $[\text{OH}^-]$ as we can see by comparing experiments 1 and 3.

19. Based on the data: can you write a **rate law** for this reaction?

$\text{Rate} = k[(\text{CH}_3)_3\text{CBr}]$

We know that it is truly a first-order reaction with respect to $(\text{CH}_3)_3\text{CBr}$ because as its concentration doubled from experiments 1 and 2, the rate also doubled.

20. Can you determine the **rate constant** for this reaction?

Let's use data from experiment 1:



$$\begin{aligned}\text{Rate} &= k[(\text{CH}_3)_3\text{CBr}] \\ 0.025 \text{ Ms}^{-1} &= k[1\text{M}] \\ 0.025 \text{ Ms}^{-1}/[1\text{M}] &= k \\ k &= 0.025 \text{ s}^{-1}\end{aligned}$$

21. Which mechanism is consistent with this empirical rate law?

Mechanism 2 because its unimolecular, rate-limiting step would give an overall rate law that is first-order in $(\text{CH}_3)_3\text{CBr}$ and zero order in OH^- , which is what the data suggests.