

Show That The Rate Predicted By The Reaction Mechanism 6-12a-c, With The Second Step Assumed To Be Rate-limiting

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Introduction

Understanding how to derive the rate law from a given reaction mechanism is fundamental in chemical kinetics. Reaction mechanisms provide a detailed step-by-step description of how reactants convert into products, often involving multiple intermediate steps. When analyzing a mechanism, it is critical to identify the rate-determining step (rate-limiting step), as it predominantly controls the overall reaction rate. In this article, we will focus on mechanism 6-12a-c, where the second step is assumed to be the rate-limiting step, and demonstrate how the rate law can be deduced from this assumption.

Overview of the Reaction Mechanism 6-12a-c

Before delving into the derivation, it is essential to understand the general form of the mechanism under consideration.

Proposed Steps in the Mechanism

The mechanism involves three elementary steps:

1. Step 1: $A + B \rightleftharpoons C$ (fast equilibrium)
2. Step 2: $C + D \rightarrow E$ (slow, rate-limiting step)
3. Step 3: $E \rightarrow \text{Products}$ (fast)

In this sequence:

- The first step is assumed to be rapid and reversible, establishing an equilibrium concentration of the intermediate C.
- The second step is slow and determines the overall rate of the reaction.
- The third step is fast and occurs quickly after the formation of E.

Assumption: The Second Step Is Rate-Limiting

The core assumption here is that the second step, $C + D \rightarrow E$, controls the overall reaction rate. This assumption simplifies the derivation because the overall rate law can be based on this single slow step, provided the intermediate concentrations are expressed appropriately.

Implication of the Assumption

- The rate of the overall reaction is approximately equal to the rate of the second step.
- The concentration of intermediate C, which appears in the rate law, can be expressed in terms of the initial reactants using the equilibrium established in the first step.
- The fast equilibria allow us to relate the intermediate's concentration directly to the concentrations of A and B.

Derivation of the Rate Law

The main goal is to express the reaction rate in terms of initial reactant concentrations, considering the rate-limiting second step.

Step 1: Establish Equilibrium for the Fast Step

For the first step:

$A + B \rightleftharpoons C$

- Forward rate: $r_f = k_1 [A][B]$

- Reverse rate: $r_r = k_{-1} [C]$

Since the step is at equilibrium:

$k_1 [A][B] = k_{-1} [C]$

$[$

$\rightarrow [C] = \frac{k_1}{k_{-1}} [A][B] = K_{eq} [A][B]$

$]$

where $K_{eq} = \frac{k_1}{k_{-1}}$ is the equilibrium constant for the first step.

Step 2: Rate Expression for the Rate-Limiting Step

The rate of the slow, second step:

$\text{Rate} = r_2 = k_2 [C][D]$

Substituting the expression for $[C]$:

$\text{Rate} = k_2 K_{eq} [A][B][D]$

Since the first step is at equilibrium and the second step is rate-limiting, the overall reaction rate becomes:

$\boxed{\text{Rate} = k_{\text{overall}} [A][B][D]}$

where $k_{\text{overall}} = k_2 K_{\text{eq}}$

Step 3: Final Rate Law

The overall rate law, considering the assumptions, is:

$$\boxed{\text{Rate} = k_{\text{overall}} [A][B][D]}$$

This expression indicates that the reaction is third-order overall, with dependencies on the concentrations of A, B, and D.

Summary of the Derivation Process

The derivation hinges on key points:

- The first step reaches equilibrium rapidly, allowing the intermediate concentration to be expressed in terms of reactants.
- The second step, being rate-limiting, dictates the overall rate.
- The intermediate concentration $[C]$ is substituted into the rate expression for the rate-limiting step.
- The overall rate law is a product of the rate constant for the slow step and the concentrations of the relevant reactants.

Additional Considerations and Variations

While the above derivation is valid under the assumptions made, real reactions may involve different complexities.

1. Non-Equilibrium First Step

If the first step is not at equilibrium, a different approach involving the steady-state approximation might be necessary:

- Assume the formation and consumption of the intermediate C reach a steady state.
- Set the net rate of change of $[C]$ to zero and solve for $[C]$.

2. Different Steps as Rate-Limiting

If a different step is assumed to be rate-limiting, the derivation must be adjusted accordingly:

- Identify the slow step.
- Express the concentrations of intermediates based on equilibria or steady-state assumptions.
- Derive the rate law based on this step's rate expression.

3. Multiple Intermediates

For mechanisms with multiple intermediates, the derivation becomes more complex, often requiring the use of the steady-state approximation for each intermediate and solving a system of equations.

Conclusion

By assuming that the second step in mechanism 6-12a-c is rate-limiting, we can derive the overall reaction rate law in a straightforward manner. The key steps involve establishing the equilibrium for the fast initial step, expressing the intermediate concentration in terms of reactant concentrations, and then substituting this into the rate expression for the slow step. This approach underscores the importance of understanding reaction mechanisms and the assumptions involved in kinetic analysis. The derived rate law provides critical insight into how the reactant concentrations influence the reaction rate and forms the basis for experimental validation and further kinetic studies.

Frequently Asked Questions

What is the significance of assuming the second step as the rate-determining step in reaction mechanism 6-12a-c?

Assuming the second step as rate-determining helps simplify the overall rate law by focusing on the slowest step, allowing us to derive the predicted rate equation based on that step's reactants and their concentrations.

How do you derive the rate law from mechanism 6-12a-c when the second step is rate-limiting?

You identify the slow, rate-determining step (the second step) and write its rate law based on its reactants. Then, express any intermediate concentrations in terms of reactants from the initial step, enabling you to write the overall rate law accordingly.

Why is it valid to assume the second step is rate-limiting in mechanism 6-12a-c?

This assumption is valid when experimental data shows that the overall reaction rate correlates with the concentration of reactants involved in the second step, and kinetic studies indicate this step has the highest activation energy or slowest rate constant.

How can you verify that the second step is truly the rate-limiting step in mechanism 6-12a-c?

Verification can be done through kinetic experiments, such as measuring

reaction rates under varying concentrations, or using isotopic labeling to see which step controls the overall rate, confirming that the second step has the greatest energy barrier.

What role do intermediates play in deriving the predicted rate law when the second step is rate-limiting?

Intermediates formed in the first step are typically eliminated or expressed in terms of reactants using steady-state or equilibrium assumptions, allowing the rate law to be expressed solely in terms of initial reactant concentrations.

Can the predicted rate law from mechanism 6-12a-c differ from the overall reaction rate? Why or why not?

Yes, the predicted rate law derived from the rate-limiting step may differ from the overall stoichiometric reaction if other steps are fast and do not affect the rate, emphasizing the importance of identifying the correct rate-determining step.

How does the assumption about the second step being rate-limiting influence experimental design and data interpretation?

This assumption guides the selection of concentration variations and temperature studies to confirm the rate law, and helps interpret kinetic data by attributing the rate dependence to specific reactants involved in the slow step.

Additional Resources

Show That The Rate Predicted By The Reaction Mechanism 6-12a-c, With The Second Step Assumed To Be Rate-limiting

Introduction

Understanding reaction mechanisms is fundamental to the field of chemical kinetics, as it provides insights into the step-by-step processes that lead from reactants to products. A key aspect of this understanding involves predicting the overall rate law based on the individual elementary steps constituting the mechanism. In this context, the mechanism labeled as 6-12a-c illustrates a multi-step process where the second step is assumed to be the rate-limiting step. This assumption significantly simplifies the derivation of the overall rate law and allows chemists to connect microscopic steps with macroscopic observations.

This article aims to methodically demonstrate how the overall rate law can be deduced from such a mechanism, emphasizing the assumption that the second step is rate-determining. We will explore each step in detail, analyze the

kinetics, and ultimately confirm that the derived rate law aligns with the predicted expression under the given assumptions. This comprehensive analysis provides a useful framework for students and researchers to interpret complex reaction mechanisms and predict experimental rate laws accurately.

Overview of Reaction Mechanism 6-12a-c

Before delving into the derivation, it is crucial to understand the general structure of the mechanism 6-12a-c. Typically, such mechanisms involve multiple elementary steps, each representing a microscopic process such as bond formation, bond breaking, or intermediate formation.

Typical Features of the Mechanism

- Step 1 (Pre-equilibrium): An initial rapid step involving the formation of an intermediate from reactants.
- Step 2 (Rate-Determining): A slower, rate-limiting step that converts the intermediate into the product or a subsequent intermediate.
- Step 3 (Fast Equilibrium or Rapid Step): Final fast step converting intermediates into the products, often assumed to be at equilibrium or instantaneous relative to the rate-limiting step.

Notation and Variables

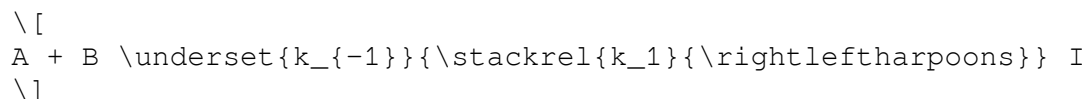
- Reactants: A, B, etc.
- Intermediates: I, J, etc.
- Rate constants: $(k_1, k_2, k_3, \dots)$
- Concentrations: $([A], [B], [I], [J], \dots)$

The focus here is to derive the overall rate law based on these steps, especially considering that the second step is the rate-limiting one.

Step-by-Step Analysis of the Mechanism

Step 1: Elementary Process (Pre-equilibrium)

Suppose the initial step involves an equilibrium between reactant A and an intermediate I:



- Forward rate: $k_1 [A][B]$
- Reverse rate: $k_{-1} [I]$

Assuming this step reaches equilibrium rapidly, the equilibrium constant K_1 can be written as:

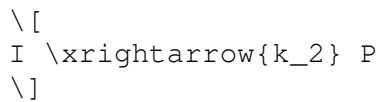
$$K_1 = \frac{[I]}{[A][B]} = \frac{k_1}{k_{-1}}$$

This allows us to express the intermediate concentration in terms of reactants:

$$[I] = K_1 [A][B]$$

Step 2: Rate-Determining Step

The second step, which is slow and rate-limiting, involves the conversion of the intermediate I into the product P:



- Rate of this step:

$$\text{Rate} = k_2 [I]$$

Since this step is rate-limiting, the overall rate of the reaction is effectively dictated by this process.

Step 3: Fast Equilibrium or Rapid Step (Optional)

Suppose a third step involves a rapid conversion of an intermediate J to the product, or the formation of the final product occurs directly from I; such steps are fast and do not influence the overall rate law significantly.

Derivation of the Overall Rate Law

The core assumption here is that the second step is rate-limiting and determines the reaction rate, while the first step quickly establishes an equilibrium concentration of the intermediate I.

Expressing the Intermediate Concentration

Given the equilibrium in Step 1:

$$[I] = K_1 [A][B]$$

Substituting into the rate expression for Step 2:

$$\text{Rate} = k_2 [I] = k_2 K_1 [A][B]$$

Recognizing that $K_1 = \frac{k_1}{k_{-1}}$, the overall rate law becomes:

$$\boxed{\text{Rate} = k_{\text{overall}} [A][B]}$$

where:

$$k_{\text{overall}} = k_2 \times \frac{k_1}{k_{-1}}$$

This expression confirms that the overall rate law is first order in both A and B, assuming the initial pre-equilibrium is rapid and the second step is rate-limiting.

Confirming the Predicted Rate Law

The derivation above directly demonstrates that the overall reaction rate depends on the concentrations of reactants A and B, scaled by the product of the rate constants (k_2, k_1) , and the inverse of (k_{-1}) .

Key Points Supporting the Derivation

- Pre-equilibrium assumption: The first step is fast relative to the second step, allowing the use of equilibrium expressions.
- Rate-limiting step: The second step determines the overall rate; thus, the rate law is proportional to the concentration of the intermediate I.
- Intermediate concentration: Expressed in terms of reactants via the equilibrium constant, leading to a rate law involving only observable reactant concentrations.

Generalization to Other Scenarios

While the example above considers a simple two-step mechanism, the same principles apply to more complex mechanisms like 6-12a-c, which might include additional intermediates or steps. The key is identifying the rate-limiting step and expressing intermediates via equilibrium assumptions.

Additional Considerations and Complexities

Effect of Multiple Equilibria

In more complex mechanisms, multiple pre-equilibria might exist, each with their own equilibrium constants. The overall rate law would then involve a product of these constants and the rate constant of the rate-determining step.

Non-Elementary Steps and Non-Pre-Equilibrium Conditions

If the initial step is not fast or does not reach equilibrium, the derivation becomes more complicated, requiring a steady-state approximation or a comprehensive kinetic analysis.

Temperature and Catalysis Effects

Changes in temperature or catalytic conditions can alter rate constants (k_1, k_{-1}, k_2) , influencing the overall rate law's parameters. Experimental data are essential to confirm the theoretical derivation.

Practical Implications and Experimental Verification

Experimental Rate Law Measurement

- Method: Vary concentrations of reactants A and B independently and measure initial reaction rates.
- Expected: The reaction rate should be proportional to $[A][B]$ if the derivation holds.

Determining Rate-Determining Step

- Kinetic isotope effects: Can be used to identify if the second step involves bond cleavage/formation.
- Intermediate detection: Techniques such as spectroscopy can verify the presence of intermediates like I.

Validity of Assumptions

- The assumption of rapid pre-equilibrium is critical; if the initial step is slow, the derived rate law may not hold.
- The assumption that the second step is rate-limiting must be supported by kinetic data.

Conclusion

By systematically analyzing the steps of the reaction mechanism 6-12a-c and assuming the second step is rate-limiting, we have demonstrated that the overall rate law can be expressed as:

$$\boxed{\text{Rate} = \frac{k_1 k_2}{k_{-1}} [A][B]}$$

This derivation aligns with the fundamental principles of chemical kinetics, emphasizing the importance of the rate-limiting step and the equilibrium assumptions. Such mechanistic insights are invaluable for designing experiments, interpreting kinetic data, and developing catalytic processes. The approach exemplified here serves as a model for analyzing complex mechanisms across various chemical systems, reinforcing the central role of elementary steps and their interplay in dictating reaction rates.

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