

Consider The Following Reaction: $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 3\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_3^-(\text{aq})$

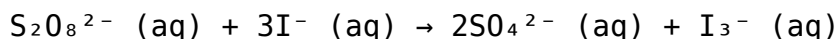
(a) The Rate Law For This

Consider The Following Reaction: $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 3\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_3^-(\text{aq})$

(a) The Rate Law For This is a fundamental question in chemical kinetics, examining how the rate of a reaction depends on the concentration of reactants. Understanding the rate law is crucial for predicting reaction behavior, designing chemical processes, and controlling reaction conditions. This reaction involves the oxidation of iodide ions (I^-) by peroxydisulfate ions ($\text{S}_2\text{O}_8^{2-}$), resulting in the formation of sulfate ions (SO_4^{2-}) and triiodide ions (I_3^-). In this article, we will explore the detailed steps to derive the rate law, analyze the reaction mechanism, and understand the factors influencing the reaction rate.

Overview of the Reaction

The chemical equation under consideration is:



This reaction is a classic example of an oxidation-reduction (redox) process, where peroxydisulfate acts as an oxidizing agent, and iodide serves as the reducing agent.

Key features:

- The reaction involves the transfer of electrons from iodide to peroxydisulfate.
- The formation of triiodide (I_3^-) is often observed as a characteristic color change and is used in kinetic studies.
- The reaction is sensitive to various factors such as concentration, temperature, and ionic strength.

Understanding Reaction Mechanism

To determine the rate law, it's essential to analyze the reaction mechanism, which involves the steps through which reactants convert into products.

Step 1: Formation of an Intermediate

The initial step generally involves the formation of an activated complex or intermediate. For this reaction, the plausible mechanism includes:

1. Generation of a reactive iodine species through the interaction of I^- with $\text{S}_2\text{O}_8^{2-}$.
2. The rate-determining step (slow step) involves the transfer of electrons from iodide to peroxydisulfate.

Step 2: Electron Transfer Process

The overall process can be simplified into:

- $\text{S}_2\text{O}_8^{2-} + \text{I}^- \rightarrow \text{SO}_4^{2-} + \text{I}^\bullet$ (or I_2)
- $2\text{I}^\bullet \rightarrow \text{I}_2$
- $\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$

In practice, the rate law hinges on the slow, rate-determining step, typically involving the initial electron transfer.

Deriving the Rate Law

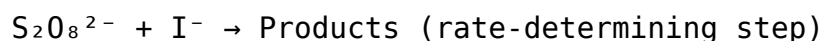
The rate law expresses how the rate depends on the concentrations of reactants involved. To derive it, we analyze the mechanism and identify the rate-determining step.

Step 1: Assumption of the Rate-Determining Step

It is generally accepted that the slowest step controls the overall rate. For this reaction, the initial electron transfer from iodide to peroxydisulfate is often rate-limiting.

Step 2: Expressing the Rate Law

Suppose the slow step involves:



The rate law for this step can be written as:

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$$

where:

- k is the rate constant,
- m and n are the orders of the reaction with respect to each reactant.

Step 3: Determining the Reaction Orders

Experimental data and kinetic studies often suggest:

- The reaction is first order in peroxydisulfate.
- The reaction is also first order in iodide.

Therefore, the overall rate law becomes:

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}]^1 [\text{I}^-]^1$$

or simply:

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

This indicates a bimolecular rate law, characteristic of a second-order overall reaction.

Experimental Techniques to Determine the Rate Law

Determining the rate law experimentally involves monitoring the concentration change over time under controlled conditions.

Methods Used:

- **Spectrophotometry:** Monitoring the formation of I_3^- by its absorbance at specific wavelengths.
- **Conductivity measurements:** Tracking ionic changes as the reaction proceeds.
- **Stopped-flow techniques:** For rapid reactions, allowing real-time observation of concentration changes.

Data Analysis:

- Plotting the natural logarithm of reactant concentration versus time to determine reaction order.
- Using initial rate methods to measure how changing concentrations affect the initial rate.

Factors Affecting the Reaction Rate

Several factors influence how quickly the reaction proceeds:

1. Reactant Concentrations

- Increasing $[S_2O_8^{2-}]$ or $[I^-]$ generally increases the rate proportionally, consistent with the first-order dependence.

2. Temperature

- Raising the temperature increases the reaction rate due to higher kinetic energy, following the Arrhenius equation.

3. Ionic Strength

- Changes in ionic strength can influence the activity coefficients, subtly affecting the rate.

4. Catalysts and Inhibitors

- While not typical for this reaction, certain catalysts can accelerate electron transfer steps.

Applications of the Rate Law in Industrial and Laboratory Settings

Understanding the rate law for this reaction has multiple practical applications:

1. Analytical Chemistry

- Quantitative determination of iodide or persulfate concentrations using kinetic methods.

2. Chemical Kinetics Studies

- Investigating electron transfer mechanisms and reaction dynamics.

3. Environmental Monitoring

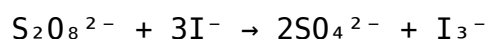
- Assessing oxidation processes in water treatment involving persulfates and halides.

4. Industrial Synthesis

- Controlling reaction conditions in processes involving iodine chemistry.

Conclusion

In summary, the reaction:



follows a bimolecular rate law expressed as:

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}][\text{I}^-]$$

This indicates that the reaction is first order with respect to each reactant and second order overall. The derivation of this rate law hinges on understanding the mechanism, identifying the rate-determining step, and confirming through experimental kinetic data. Recognizing how various factors

influence this rate allows chemists to control and optimize such reactions in laboratory and industrial settings.

Understanding the kinetics of this reaction not only deepens our comprehension of redox processes but also enhances our ability to manipulate reactions for desired outcomes. Whether in analytical applications, environmental chemistry, or industrial synthesis, grasping the principles behind the rate law is invaluable for advancing chemical science.

Keywords: reaction kinetics, rate law, $\text{S}_2\text{O}_8^{2-}$, I^- , reaction mechanism, electron transfer, chemical kinetics, experimental methods, reaction rate factors

Frequently Asked Questions

What is the overall reaction involved in the oxidation of iodide by persulfate?

The overall reaction is $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 3\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_3^-(\text{aq})$.

How can the rate law for the reaction between $\text{S}_2\text{O}_8^{2-}$ and I^- be determined?

The rate law can be determined experimentally by measuring how the reaction rate varies with the concentrations of $\text{S}_2\text{O}_8^{2-}$ and I^- , often using initial rate methods.

What is the expected form of the rate law for this reaction?

The rate law is typically expressed as $\text{rate} = k [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$, where m and n are the reaction orders with respect to each reactant.

Based on known mechanisms, what are the likely reaction orders for $\text{S}_2\text{O}_8^{2-}$ and I^- ?

The reaction is often first order in both $\text{S}_2\text{O}_8^{2-}$ and I^- , making it overall second order, but experimental determination is necessary for confirmation.

What experimental techniques are used to determine the rate law of this reaction?

Techniques include monitoring concentration changes over time using

spectrophotometry or titration, and performing initial rate experiments at varying reactant concentrations.

Why is understanding the rate law important in this reaction?

Knowing the rate law helps in understanding the reaction mechanism, predicting reaction behavior, and designing appropriate reaction conditions.

What role does the I_3^- ion play in the reaction mechanism?

I_3^- is the product formed from the oxidation of I^- , and its formation rate can be used to monitor the reaction progress, providing insights into the mechanism and rate law.

Additional Resources

Consider The Following Reaction: $S_2O_8^{2-} (aq) + 3I^- (aq) \rightarrow 2SO_4^{2-} (aq) + I_3^- (aq)$

Understanding the Rate Law for the Reaction

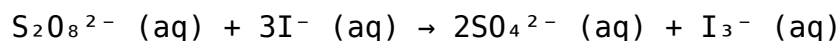
In the realm of chemical kinetics, deciphering how fast a reaction proceeds and what influences its rate is fundamental. The reaction between persulfate ions ($S_2O_8^{2-}$) and iodide ions (I^-) serves as a classic example often studied in advanced chemistry courses, illustrating key principles of reaction mechanisms and rate laws. This reaction is not only academically intriguing but also practically important, as it underpins processes in analytical chemistry, environmental science, and industrial applications.

This article aims to explore the detailed aspects of this reaction, focusing on how to determine its rate law—a mathematical expression that relates the reaction rate to the concentrations of the reactants. We will delve into the reaction's mechanistic pathway, how experimental methods reveal its kinetic order, and what factors influence its rate, all presented in a clear, reader-friendly manner.

Understanding the Chemical Reaction

Reaction Overview

The chemical equation under consideration is:



Breaking down the reactants and products:

- $\text{S}_2\text{O}_8^{2-}$ (persulfate ion): A strong oxidizing agent capable of accepting electrons during oxidation processes.
- I^- (iodide ion): A reducing agent that donates electrons, getting oxidized in the process.
- SO_4^{2-} (sulfate ion): A stable oxidation product resulting from the reduction of persulfate.
- I_3^- (triiodide ion): Formed when iodine molecules (I_2) generated during the reaction combine with excess I^- .

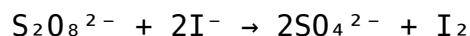
This reaction is classified as an oxidative redox process, where $\text{S}_2\text{O}_8^{2-}$ oxidizes I^- to I_2 , which then interacts with I^- to form I_3^- .

Mechanistic Pathway of the Reaction

Understanding the step-by-step mechanism helps elucidate how the rate law is derived. The proposed mechanism involves two primary steps:

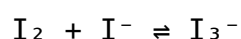
1. Rate-Determining Electron Transfer:

$\text{S}_2\text{O}_8^{2-}$ reacts with I^- to produce I_2 and sulfate ions:



2. Fast Equilibrium Formation of I_3^- :

The generated I_2 reacts rapidly with excess I^- to form I_3^- :



The overall reaction combines these steps, with the first step typically being rate-limiting, implying that the overall rate depends mainly on the concentrations of $\text{S}_2\text{O}_8^{2-}$ and I^- .

Determining the Rate Law: Experimental Approach

Concept of Rate Laws

A rate law expresses how the rate of a reaction depends on the concentrations of the reactants. For this reaction, a general form can be written as:

$$\text{Rate} = k [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n$$

where:

- k is the rate constant
- m and n are the reaction orders with respect to $S_2O_8^{2-}$ and I^- , respectively

The goal is to determine the values of m and n through carefully designed experiments.

Methodology for Kinetic Studies

To find the reaction orders, chemists typically perform a series of controlled experiments where they vary the concentration of one reactant while keeping the other constant. The steps include:

1. Prepare multiple reaction mixtures with different known concentrations of $S_2O_8^{2-}$ and I^- .
2. Monitor the reaction progress by measuring the formation of I_3^- over time. This can be done spectrophotometrically, as I_3^- has a characteristic absorbance.
3. Determine the initial reaction rates by measuring the change in I_3^- concentration during the initial phase of the reaction.
4. Analyze the data to deduce the reaction orders:
 - If doubling $[S_2O_8^{2-}]$ while keeping $[I^-]$ constant doubles the rate, the order with respect to $S_2O_8^{2-}$ is 1.
 - Similarly, observe how changes in $[I^-]$ affect the rate to find the order n .

Through such systematic experimentation, the reaction's kinetic parameters are elucidated.

The Derived Rate Law for the Reaction

Based on experimental findings and mechanistic reasoning, the rate law for the persulfate-iodide reaction is generally expressed as:

$$\text{Rate} = k [S_2O_8^{2-}]^1 [I^-]^2$$

This indicates:

- First-order dependence on persulfate ions ($S_2O_8^{2-}$)
- Second-order dependence on iodide ions (I^-)

Implication: The reaction rate increases linearly with increasing persulfate concentration but quadratically with iodide concentration, highlighting the significant influence of I^- on reaction speed.

Factors Affecting the Reaction Rate

Several factors can influence the overall rate of this redox process:

1. Concentration of Reactants:

As shown, increasing $[S_2O_8^{2-}]$ or $[I^-]$ accelerates the reaction, in accordance with the rate law.

2. Temperature:

Higher temperatures generally increase kinetic energy, leading to faster reaction rates. The relationship is described by the Arrhenius equation:

$$k = A e^{(-E_a/RT)}$$

where E_a is the activation energy, R the gas constant, and T the temperature.

3. Presence of Catalysts:

Certain catalysts can lower the activation energy, thus speeding up the reaction without being consumed.

4. pH of the Solution:

Although not directly involved in the rate law, pH can influence reaction pathways, especially in aqueous systems where protonation states matter.

5. Light and External Influences:

Exposure to light can sometimes induce photochemical pathways, altering reaction rates.

Practical Applications and Significance

Understanding the kinetics and rate law of this reaction has practical importance:

- Analytical Chemistry: The reaction underpins iodine titrations, a method for determining halide concentrations.
- Environmental Monitoring: Persulfate-based oxidation is used in wastewater treatment to degrade organic pollutants.
- Industrial Processes: Controlled oxidation reactions utilize this mechanism for various syntheses.

Moreover, knowing how to manipulate reaction conditions enables chemists to optimize processes for efficiency and safety.

Conclusion: The Significance of Kinetic Understanding

The reaction between persulfate and iodide exemplifies how detailed kinetic analysis informs our understanding of complex chemical processes. By dissecting the mechanistic steps, designing experiments to measure reaction rates, and deriving the rate law, chemists gain insight into how molecules interact in solution. The established rate law—first-order in persulfate and second-order in iodide—not only helps predict how the reaction proceeds under different conditions but also guides practical applications across various scientific fields.

In essence, the study of this reaction underscores the broader importance of kinetics in chemistry: revealing the invisible dance of molecules that dictates the speed and outcome of reactions vital to science and industry alike.

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