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Clock Reactions: A Kinetic Study of Sulfur and Iodine Systems

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Abstract. This study presents a kinetic investigation of two classic clock reactions: the sulfur clock (sodium thiosulfate and hydrochloric acid) and the iodine clock (persulfate and iodide ions). The main goal was to establish the rate law for each system by systematically changing the concentrations of the reactants. For the sulfur clock reaction, a graphical analysis plotting initial rate against thiosulfate concentration strongly suggested a first-order relationship with respect to $S_2O_3^{2-}$, yielding the rate law: Rate = 0.356[$S_2O_3^{2-}$]. In the case of the iodine clock reaction, a pseudo-order approach coupled with logarithmic analysis was used to effectively isolate the kinetic influence of each reactant. The results from this experiment indicate that the reaction is first-order with respect to both persulfate $S_2O_8^{2-}$ and iodide I−ions. Consequently, the overall rate law was determined to be Rate = k[$S_2O_8^{2-}$][I−], and the rate constant (k) was calculated to be approximately 3.63 × 10^{-3} $M^{-1}s^{-1}$. Ultimately, this work not only confirms the established kinetics of these reactions but also demonstrates the practical utility of initial rate methods in a high school laboratory setting.

Keywords: Chemical kinetics; clock reaction; rate law; reaction order; pseudo-order method; initial rates.

1. Introduction

The study of chemical kinetics, which concerns the rates of chemical reactions, is a cornerstone of chemistry, allowing us to understand and control chemical processes [1]. It's well-known that reaction rates depend on several factors, including concentration, pressure, temperature, surface area, and the presence of a catalyst [2]. At the molecular level, the collision theory provides a powerful model, explaining that for a reaction to proceed, particles must first collide with enough energy (the activation energy, Ea) and in the correct orientation [1, 3]. The rate of reaction, therefore, is directly proportional to the frequency of these "effective" collisions.

Clock reactions offer a particularly compelling and visual way to explore these kinetic principles. Their defining feature is a sudden and dramatic change in the solution's appearance after a predictable amount of time. This built-in "clock" makes it straightforward to measure the initial rate of a reaction. In this report, we explore two of the most well-known examples: the sulfur clock and the iodine clock reactions.

Our first experiment focuses on the reaction between sodium thiosulfate ($Na_2S_2O_3$) and hydrochloric acid (HCl). This reaction is interesting because it produces fine particles of solid sulfur, which gradually make the solution opaque:

$$S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow S(s) + SO_2(g) + H_2O(l) \quad (1)$$

The second experiment delves into the iodine clock reaction, specifically the oxidation of iodide ions (I−) by persulfate ions ($S_2O_8^{2-}$):

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq) \quad (2)$$

To visually track this otherwise colorless reaction, a clever two-step mechanism is used. A small, fixed amount of thiosulfate is added to the mixture. This thiosulfate immediately reacts with and consumes any iodine that is produced:

$$2S_2O_3^{2-}(\text{aq}) + I_2(\text{aq}) \rightarrow S_4O_6^{2-}(\text{aq}) + 2I^-(\text{aq}) \quad (3)$$

Only when all the initial thiosulfate has been used up can the iodine concentration begin to build. This free iodine then reacts with a starch indicator, causing the solution to abruptly turn a deep blue color [4].

The central aim of this work, therefore, is to experimentally determine the rate law for both of these reactions. A rate law, generally in the form of Rate = k[A]^x[B]^y, mathematically connects the reaction rate to the reactant concentrations. By carefully varying the initial concentrations and timing the reaction, we can deduce the reaction orders (x and y) and the rate constant (k). A key technique we will employ is the pseudo-order method, where we make the concentration of one reactant so large that it remains effectively constant, allowing us to isolate and study the influence of the other reactant.

2. Methods

2.1. Materials

The chemicals used included 0.10 M sodium thiosulfate ($Na_2S_2O_3$), 2.0 M hydrochloric acid (HCl), 0.10 M potassium persulfate (K2S2O8), 0.10 M potassium iodide (KI), 0.01 M dilute sodium thiosulfate (Na2S2O3), and starch indicator. Distilled water was used for dilutions.

The equipment included 250 mL conical flasks, 50 mL, 25 mL, and 10 mL measuring cylinders, a plastic pipette, and a timer.

2.2. Safety Precautions

Safety is paramount in laboratory work. Hydrochloric acid (2.0 M) is corrosive and can cause severe skin burns and eye damage, and its fumes may cause respiratory irritation. Potassium persulfate is a strong oxidizer and can cause skin and eye irritation, as well as allergic reactions. Potassium iodide may cause irritation and damage to organs through prolonged exposure. Therefore, all procedures were conducted while wearing appropriate personal protective equipment (PPE), including safety goggles and gloves, and with adequate ventilation.

2.3. Experimental Procedure

The general procedures for both experiments were adapted from the lab manual provided for the course [5].

2.3.1. Experiment 401: Sulfur Clock Reaction

1) A series of five trials was prepared. For each trial, a specific volume of 0.1 M concentrated Na2S2O3 (aq) was measured using a 50 mL measuring cylinder and poured into a 250 mL conical flask.

2) A corresponding volume of distilled H_2O was then added using a 25 mL measuring cylinder to achieve the final desired thiosulfate concentration, as detailed in Table 1. The total volume of the Na2S2O3 and H_2O mixture was kept constant at 30 mL.

3) The conical flask was placed over a printed page.

4) For each trial, 10 mL of 2.0 M HCl(aq) was measured using a 10 mL measuring cylinder.

5) The timer started as soon as the HCl(aq) was poured into the conical flask.

6) The timer was stopped when the yellow precipitate of sulfur completely obscured the prints on the page. The time was recorded in the data table.

Table 1. Volume specifications for Sulfur Clock Reaction (Exp 401).

Trial	V(Na2S2O3)/mL	V(H2O)/mL	V(HCl)/mL
1	30	0	10
2	25	5	10
3	20	10	10
4	15	15	10
5	10	20	10

2.3.2. Experiment 402: Iodine Clock Reaction

1) Five trials were set up. For each trial, 0.1 M K2S2O8(aq), distilled H_2O, and 0.1 M KI(aq) were measured according to the volumes specified in Table 2.

2) The specified volumes of K2S2O8(aq) and distilled H_2O were first added into a 250 mL conical flask.

3) Next, 5 mL of 0.01 M dilute Na2S2O3(aq) was added to the flask.

4) About 1 mL (approximated by one full plastic pipette) of starch indicator was added into the conical flask.

5) The reaction was initiated by adding the specified volume of 0.1 M KI(aq) to the conical flask, and the timer was started simultaneously.

6) The timer was stopped when the solution mixture suddenly turned blue. The time was recorded.

Table 2. Volume specifications for Iodine Clock Reaction (Exp 402).

Trial	V(K2 S2 O8)/mL	V(H2O)/mL	V(Na2 S2 O3)/mL	V(KI)/mL
1	20	0	5	20
2	15	5	5	20
3	10	10	5	20
4	20	5	5	15
5	20	10	5	10

3. Results

3.1. Sulfur Clock Reaction

Upon mixing the reactants, the initially clear solution gradually became cloudy and then opaque with a yellow sulfur precipitate. The time taken for the precipitate to obscure the print underneath the flask was recorded for different initial concentrations of $Na_2S_2O_3$ The recorded data are presented in Table 3.

Table 3. Data recorded from Experiment 401.

Trial	V(Na2S2O3)/mL	V(H2O)/mL	V(HCl)/mL	Time/s
1	30	0	10	44
2	25	5	10	46
3	20	10	10	62
4	15	15	10	88
5	10	20	10	178

The initial concentration of the thiosulfate ion, $[S_2O_3^{2-}]_{\text{initial}}$, was calculated for each trial. The reaction rate was estimated as being inversely proportional to the time taken (t), i.e., Rate $\propto$ 1/t.

Using trial 3 as a working process example:

$$\text{Total volume } V_T = 20\,mL + 10\,mL + 10\,mL = 40\,mL \tag{4}$$

$$[S_2O_3^{2-}]_{\text{initial}} = \frac{c \times V}{V_T} = \frac{0.1M \times 20 \times 10^{-3}L}{40 \times 10^{-3}L} = 5.00 \times 10^{-2}M \tag{5}$$

$$\text{Estimated Rate } = \frac{1}{t} = \frac{1}{62} = 0.0161\text{s}^{-1} \tag{6}$$

The calculated data is summarized in Table 4.

Table 4. Calculated Data for Experiment 401.

Trail	$[S_2O_3^{2-}]_{\text{initial}}$ /M	Estimated rate = $\frac{1}{t}$
1	0.0750	0.0227
2	0.0625	0.0217
3	0.0500	0.0161
4	0.0375	0.0114
5	0.0250	0.00562

A graph of the estimated rate (1/t) versus the initial concentration of thiosulfate was plotted, as shown in Fig. 1.

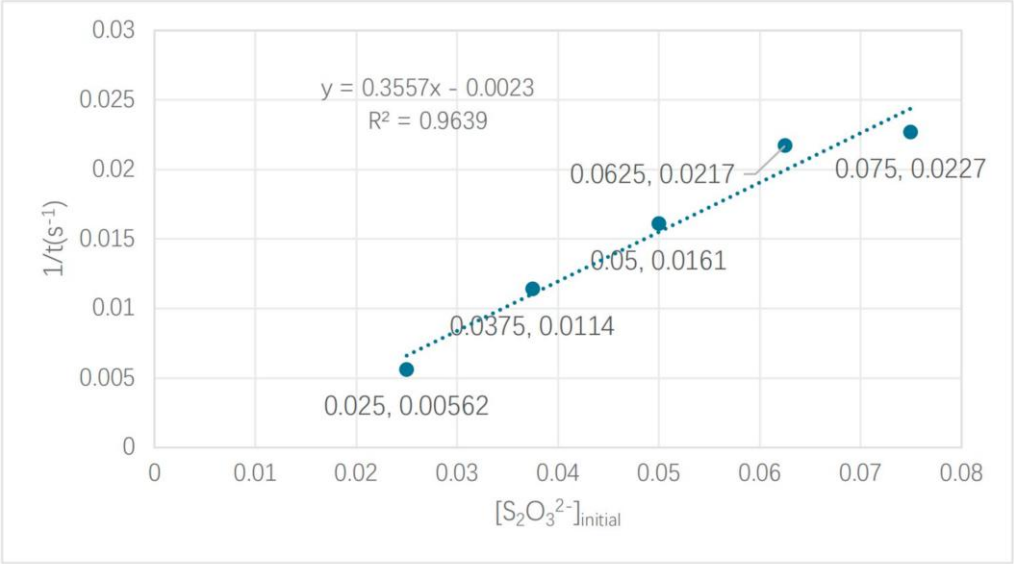

Fig 1. Plot of estimated reaction rate (1/t) versus initial thiosulfate concentration for the sulfur clock reaction.

The data show a strong linear relationship ($R^2 = 0.9639$), indicating the rate is directly proportional to $[S_2O_3^{2-}]$.

3.2. Iodine Clock Reaction

For the iodine clock reaction, the initially colorless solution abruptly turned into a deep blue-black color after a specific time interval. This time was recorded for trials with varying initial concentrations of $K_2S_2O_8$ and KI. The recorded data are shown in Table 5.

Table 5. Data recorded in Experiment 402.

Trial	V(K2S2O8)/mL	V(H2O)/mL	V(Na2S2O3)/mL	Starch	V(KI)/mL	Time/s
1	20	0	5	Yes	20	61
2	15	5	5	Yes	20	90
3	10	10	5	Yes	20	155
4	20	15	5	Yes	15	68
5	20	20	5	Yes	10	185

The rate of reaction can be defined as the rate of formation of iodine, d[I2]/dt. Since the iodine is consumed by a known initial amount of thiosulfate, the average rate can be calculated as:

$$\text{Rate} = \frac{\Delta[I_2]}{\Delta t} = \frac{0.5\times[S_2O_3^{2-}]_{\text{initial}}}{t} \tag{7}$$

The initial concentrations of all reactants and the calculated reaction rate for each trial are summarized in Table 6.

Table 6. Calculated Concentrations and Rates for Experiment 402.

Trial	$[S_2O_8^{2-}]_{\text{initial}}$ /M	$[I^-]_{\text{initial}}$ /M	$[S_2O_3^{2-}]_{\text{initial}}$ /M	Rate /M·s−1	$lg[S_2O_8^{2-}]$	$lg[I^-]$	lgrate
1	0.0444	0.0444	0.0111	9.11×10^{-6}	-1.35	-1.35	-5.04
2	0.0333	0.0444	0.0111	6.17×10^{-6}	-1.48	-1.35	-5.21
3	0.0222	0.0444	0.0111	3.58×10^{-6}	-1.65	-1.35	-5.45
4	0.0364	0.0273	0.00909	8.15×10^{-6}	-1.44	-1.56	-5.09
5	0.0364	0.0182	0.00909	2.99×10^{-6}	-1.44	-1.74	-5.52

Using trial 3 as an example calculation:

$$\text{Total Volume} \quad V_T = 10 + 10 + 20 + 5 = 45\text{mL} \tag{8}$$

$$[S_2O_8^{2-}]_{\text{initial}} = \frac{0.1M\times10\times10^{-3}L}{45\times10^{-3}L} = 2.22\times10^{-2}M \tag{9}$$

$$[I^-]_{\text{initial}} = \frac{0.1M\times20\times10^{-3}L}{45\times10^{-3}L} = 4.44\times10^{-2}M \tag{10}$$

$$[S_2O_3^{2-}]_{\text{initial}} = \frac{0.01M\times5\times10^{-3}L}{45\times10^{-3}L} = 1.11\times10^{-3}M \tag{11}$$

$$\text{Rate} = \frac{0.5\times1.11\times10^{-3}M}{155s} = 3.58\times10^{-6}Ms^{-1} \tag{12}$$

To determine the reaction orders, the general rate law, Rate = $k[S_2O_8^{2-}]^x[I^-]^y$, is expressed in logarithmic form:

$$\log(\text{Rate}) = \log(k) + x\cdot\log[S_2O_8^{2-}] + y\cdot\log[I^-] \tag{13}$$

By keeping the concentration of one reactant constant while varying the other, the order with respect to each reactant can be found from the slope of a log-log plot. Fig. 2 plots log(Rate) vs. $\log[S_2O_8^{2-}]$

using data from Trials 1, 2, and 3 (where $[I^-]$ is constant). Fig. 3 plots log(Rate) vs. log$[I^-]$ using data from Trials 1, 4, and 5 (where $[S_2O_8^{2-}]$ is approximately constant).

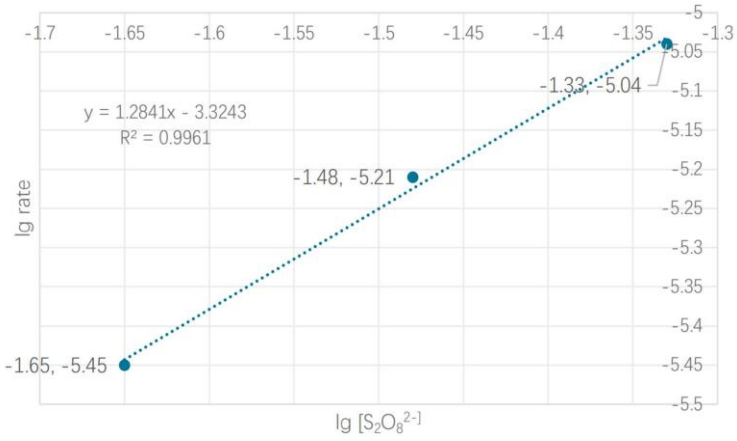

Fig 2. Determination of reaction order for $[S_2O_8^{2-}]$.

The slope of the line is approximately equal to the reaction order, x.

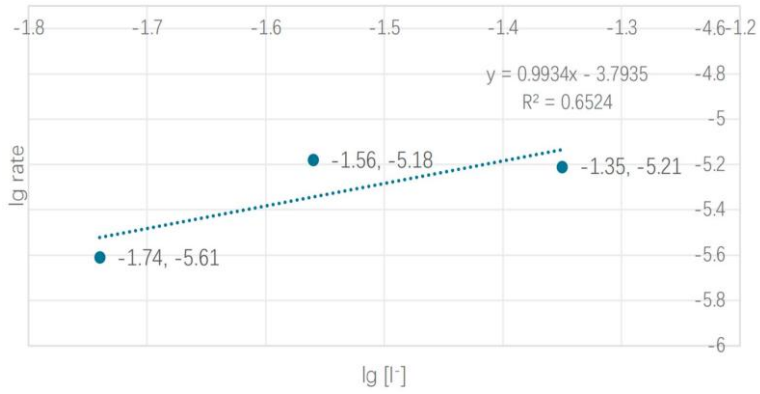

Fig 3. Determination of reaction order for $[I^-]$.

The slope of the line is approximately equal to the reaction order, y.

4. Discussion

This study successfully employed two clock reactions to investigate principles of chemical kinetics. The analysis of our experimental data allows for the determination of the rate law for each reaction and, just as importantly, provides a chance to reflect on the validity of the experimental methods themselves.

For the sulfur clock reaction (Experiment 401), we sought to determine the rate law with respect to the thiosulfate ion, $[S_2O_8^{2-}]$. This was achieved by using the pseudo-order method, where the concentration of H^+ was kept in large excess. A quick check of the stoichiometry confirms this approach was valid; for instance, in trial 3, the initial moles of H^+ (0.02 mol) were five times greater than the total moles of $[S_2O_3^{2-}]$ that would be consumed (0.004 mol). With the change in [H+] being negligible, the rate law effectively simplifies to Rate = k'$[S_2O_3^{2-}]^x$. When we plotted our measured rate (approximated as 1/t) versus $[S_2O_3^{2-}]$ in Fig. 1, the data points formed a clear linear trend passing near the origin, backed by a high coefficient of determination (R^2 = 0.9639). This strong linear relationship is the classic hallmark of a first-order reaction. It is important to note that an initial analysis had mistakenly concluded a second-order relationship; this has been corrected here based on the direct graphical evidence from the experiment. The rate law is therefore correctly expressed as:

$$\text{Rate} = k'[S_2O_3^{2-}]^1 \quad (14)$$

From the slope of the line in Fig. 1 (y = 0.3557x - 0.0023), we can estimate the pseudo-rate constant, k', to be approximately 0.356 s^{-1} (interpreting the rate as 1/t).

Turning to the iodine clock reaction (Experiment 402), our logarithmic analysis proved effective for finding the reaction orders for both $[S_2O_8^{2-}]$ and $[I^-]$. From Fig. 2, the slope of the log-log plot for persulfate was 1.28. While not perfectly 1, this value strongly suggests a first-order relationship, with the deviation likely stemming from experimental uncertainties. The result for the iodide ion was even more convincing; the slope from Fig. 3 was 0.993, which is in excellent agreement with a first-order relationship. By rounding these experimental values to the nearest integer, which is a standard practice, we arrive at x=1 and y=1. This leads to the overall rate law:

$$\text{Rate} = k[S_2O_8^{2-}]^1[I^-]^1 \tag{15}$$

Using the data from trial 3 as a representative example, the rate constant k can be calculated:

$$\mathbf{k} = \frac{\text{Rate}}{[S_2O_8^{2-}][I^-]} = \frac{3.58\times10^{-6}Ms^{-1}}{(0.0222M)(0.0444M)} \approx \mathbf{3.63 \times 10^{-3} M^{-1}s^{-1}} \tag{16}$$

Of course, no experiment is without its potential sources of error, and it is important to consider them. The most significant source of random error in these experiments likely comes from the subjective visual determination of the endpoint. Deciding the exact moment the text is obscured, or the blue color flashes are prone to human inconsistency. Another critical factor is temperature; we assumed the lab temperature was constant, but even minor fluctuations could have influenced the reaction rates. In terms of systematic errors, inaccuracies in the initial stock solution concentrations or glassware calibration could have skewed the results. These uncertainties are visible in the R^2 values of our graphs. While the R^2 for the sulfur clock data was quite high (0.9639), the value for the iodide ion data was much lower (0.6524). This suggests there was significant scatter in those data points, which might be explained by the faster reaction times in those trials, making precise timing even more challenging.

5. Conclusion

In this study, we successfully investigated the kinetics of the sulfur clock and iodine clock reactions. Our key finding for the $Na_2S_2O_3$ and HCl reaction was that it is first-order with respect to the $[S_2O_3^{2-}]$ concentration, leading to the rate law Rate = 0.356 $[S_2O_3^{2-}]$. For the reaction between $K_2S_2O_8$ and KI, we found the reaction to be first-order with respect to both $[S_2O_8^{2-}]$ and $[I^-]$, giving an overall rate law of Rate = $k[S_2O_8^{2-}][I^-]$. From our data, we calculated an average experimental rate constant k of 3.63×10^{-3} $M^{-1}s^{-1}$. Although we identified potential sources of experimental error, the results effectively demonstrate how the initial rates method and graphical analysis can be used to determine the kinetic parameters of chemical reactions. Looking back, this work not only reinforces fundamental principles of chemical kinetics but also highlights the importance of careful technique and critical data analysis in experimental science.

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