

Determination of Reaction Orders in the Iodine Clock by a Clock-Time Method.

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I. Abstract

A clock-time method was used to determine the reaction orders and rate constant for the iodine clock system under constant-volume, fixed-condition experiments. Log–log fits of $\frac{1}{t}$ versus initial concentration gave orders $m = 0.5939$ in H_2O_2 and $n = 0.8755$ in I^- , with a pooled rate constant $k = 1.113 \pm 0.091 \text{ s}^{-1} \text{ M}^{-1.47}$. The dataset was limited by single runs, a narrow concentration span, subjective visual endpoints and uncontrolled temperature, which likely inflated uncertainty. Despite these constraints, the quantified rate law enables practical tuning of benign timing elements relevant to Ordnance, Munitions and Explosives and provides a basis for improved measurements using photometric endpoints, thermostatted operation and initial-rate methods.

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1. Aim

The reaction orders in hydrogen peroxide and iodide for the iodine clock system were to be determined, and the rate constant was to be evaluated under fixed experimental conditions using the clock-time method. A secondary aim was to illustrate how empirical kinetics can inform timing elements relevant to Ordnance, Munitions and Explosives (OME).

2. Hypothesis

It was hypothesised that the time to the first permanent blue colour, t , would be inversely proportional to the initial rate of iodine formation [1]. Accordingly, increasing the initial concentration of any reactant present in the rate law would be expected to decrease t and increase $1/t$. Linear relations were therefore anticipated between $\log_{10}(1/t)$ and $\log_{10}[\text{reactant}]_0$, with slopes equal to the corresponding reaction orders [2].

3. Variables

Independent: Part 1—initial $[\text{H}_2\text{O}_2]_0$, Part 2—initial $[\text{I}^-]_0$.

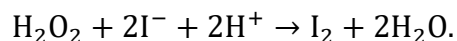
Dependent: Clock time $t(\text{s})$ and reciprocal $1/t(\text{s}^{-1})$.

Controlled: Temperature, acidity, vitamin C concentration, starch concentration, glassware, timing protocol; in both parts the total volume was fixed at 25.0 mL.

4. Theory

4.1. Concepts, equations and definitions

In acidic solution, hydrogen peroxide oxidises iodide to iodine:



Vitamin C reduces I_2 back to I^- until the reductant is exhausted; once consumed, free iodine accumulates and forms the blue iodine–starch complex [3]. Because a fixed iodine threshold triggers the visible change, the elapsed time acts as a clock inversely proportional to the initial rate. The empirical rate expression used is:

$$\frac{1}{t} = k [\text{H}_2\text{O}_2]^m [\text{I}^-]^n.$$

For parameter estimation, $\log_{10}(1/t)$ was regressed on $\log_{10}[\text{reactant}]_0$ using ordinary least squares (OLS).

4.2. Importance of Kinetics in OME

Kinetic characterisation can estimate delay and timing management in OME. A benign chemical delay element can be tuned by concentration control. Using the present scaling's (as per 7. Derived rate law), doubling $[\text{I}^-]_0$ shortens the delay by $2^{0.88} \approx 1.84$, whereas a 50% increase in $[\text{H}_2\text{O}_2]_0$ shortens it by $1.5^{0.59} \approx 1.30$. Such levers allow a nominal 30s delay to be adjusted while temperature and acidity are held fixed [4].

5. Calculations

5.1. Stock Concentration Conversion

Using 3% (w/w) means 3.00g H₂O₂ per 100ml of solution:

$$n_{\text{H}_2\text{O}_2} = \frac{m}{M_r} = \frac{3.00}{34.01} = 0.0882 \text{ mol (in 100 mL)}$$

Per litre:

$$[\text{H}_2\text{O}_2]_{\text{stock}} = \frac{0.0882 \text{ M}}{0.100 \text{ L}} \times \frac{0.100}{1.000} = 0.882 \text{ Mol L}^{-1} = 0.88 \text{ M}$$

5.2. Initial Concentration by Dilution

For any species X delivered from a stock $C_{X,\text{stock}}$ at volume V_X into a mixture of total volume V_{tot} :

$$[X]_0 = \frac{C_{X,\text{stock}} V_X}{V_{\text{tot}}} \text{ (with } V \text{ in L or mL consistently).}$$

Worked example (Part 1, Trial I.2):

$$[\text{H}_2\text{O}_2]_0 = \frac{0.88 \times 2.0}{25.0} = 0.0704 \text{ M}; [\text{I}^-]_0 = \frac{0.20 \times 3.0}{25.0} = 0.02400 \text{ M.}$$

5.3. Transformations used for regression

$$y = \log_{10} \left(\frac{1}{t} \right), x = \log_{10} [\text{reactant}]_0.$$

The fitted OLS line is $y = a + bx$. For Part 1, $b = m$ (order in H₂O₂); for Part 2, $b = n$ (order in I⁻). The intercept $a = \log_{10} k'$ is a pseudo-constant for each series.

5.4. Computing the overall rate constant k

From the empirical rate law,

$$k = \frac{1/t}{[\text{H}_2\text{O}_2]^m [\text{I}^-]^n}.$$

Worked example (Part 2, Trial II.3):

$$\begin{aligned} t &= 90\text{s}, \frac{1}{t} = 0.011111\text{ s}^{-1} \\ [\text{H}_2\text{O}_2]_0 &= 0.1056\text{ M}, [\text{I}^-]_0 = 0.02400 \\ k &= \frac{0.011111}{(0.1056)^{0.5939} (0.02400)^{0.8755}} = 1.106\text{ s}^{-1}\text{ M}^{-1.47}. \end{aligned}$$

The pooled estimate (mean $\pm$ sample standard deviation) was $k = 1.113 \pm 0.091\text{s}^{-1}\text{ M}^{-1.47}$ with relative standard deviation (RSD) = 8.2% (this was calculated as the sample standard deviation divided by the mean, multiplied by 100%, using the per-trial k values from Parts 1 and 2: sections **6.1**, **6.2**).

6. Data & Observations

6.1. Part 1: Order in $[\text{H}_2\text{O}_2]$

Trial	$[\text{H}_2\text{O}_2]$ (M)	t (s)	$1/t$ (s^{-1})	$\log_{10}[\text{H}_2\text{O}_2]$	k ($\text{s}^{-1}\text{ M}^{-1.47}$)
I.1	0.03520000	167	0.00598802	-1.453457	1.144
I.2	0.07040000	131	0.00763359	-1.152427	0.967
I.3	0.10560000	88	0.01136364	-0.976336	1.131
I.4	0.14080000	75	0.01333333	-0.851397	1.119

6.2.Part 2: Order in $[I^-]$

Trial	$[I^-]_0$ (M)	t (s)	$1/t$ (s^{-1})	$\log_{10}[I^-]_0$	k ($s^{-1} M^{-1.47}$)
II.1	0.00800000	215	0.00465116	-2.096910	1.211
II.2	0.01600000	142	0.00704225	-1.795880	1.000
II.3	0.02400000	90	0.01111111	-1.619789	1.106
II.4	0.03200000	63	0.01587302	-1.494850	1.228

7. Results & Observations

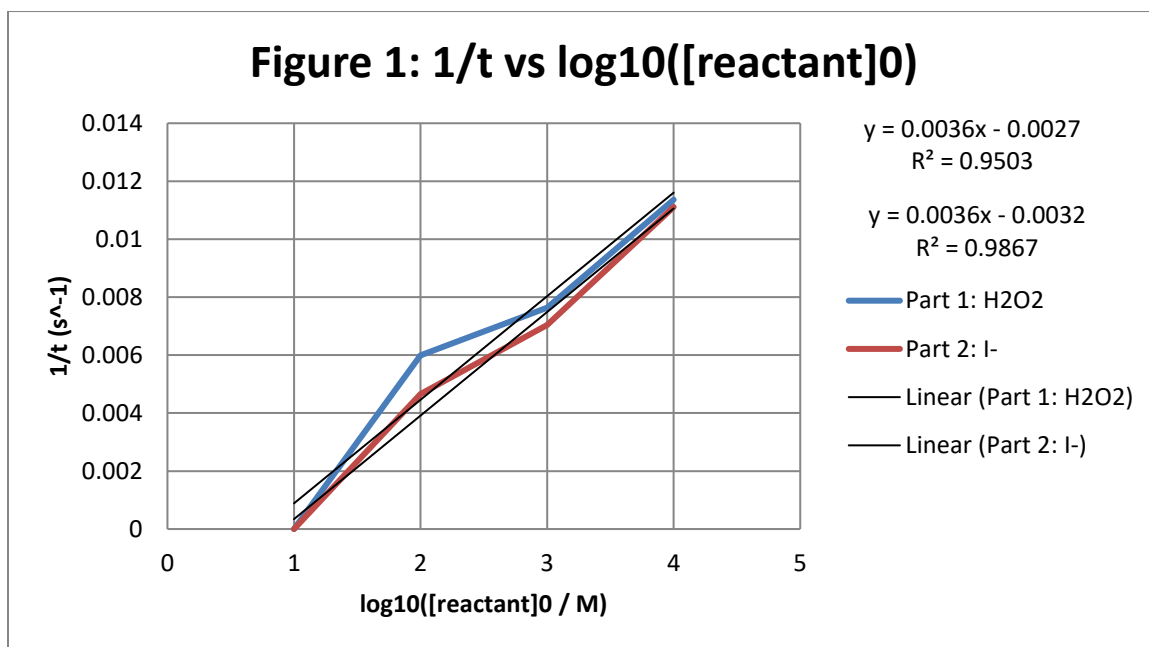


Figure 1 - versus $\log_{10}[\text{reactant}]_0$ for both parts

Goodness of fit and orders: Linear fits were strong (Part 1 $R^2 = 0.953$, Part 2 $R^2 = 0.968$) with no trend in residuals. The order in hydrogen peroxide was $m = 0.5939$ (fractional) and in iodide $n = 0.8755$ (near first order). The rate law:

$$\text{Rate} = k [H_2O_2]^{0.59} [I^-]^{0.88}$$

described the data within the tested ranges. Per-trial k values were consistent (relative standard deviation $\approx 8\%$).

7.1. What is weak in the data

Single runs per condition: Each concentration level was recorded once. Without replicates there is no direct estimate of within-condition variance, so the standard errors on slopes and intercepts are optimistic. A single mistimed endpoint can shift the slope noticeably because there are only four points per series [5].

Narrow dynamic range: Each series spans only a $\sim 4\times$ concentration range and roughly a $2\text{--}3\times$ change in $1/t$. Slopes from such short baselines are sensitive to small timing or concentration errors; leverage from the end points is high [6].

Potential heteroscedasticity: Timing precision is worse at short times (mixing and reaction overlap) and at very long times (operator drift). Residuals were visually even, but with $n = 4$ this cannot be tested reliably, unequal variance would bias ordinary least squares.

Endpoint definition: “First permanent blue” is subjective and operator-dependent.

Small differences ($\approx 1\text{--}2$ s) matter when t is 60–90 s. Rounding to whole seconds introduces quantisation error that propagates in $1/t$ and $\log_{10}\left(\frac{1}{t}\right)$ [5].

Mixing dead time: The clock starts when reagents contact, not when the mixture is homogeneous. Variable dead time adds a run-specific offset to t , bending the log–log relationship if it changes with condition [5].

7.2.Mitigation methods

Photometric endpoint: Replace the visual call with a fixed absorbance threshold using a colorimeter or simple LED/photodiode at the iodine–starch band. This removes operator bias, reduces second-level jitter, and produces continuous time stamps for better regression [7].

Thermostating and logging: Run in a water bath at a fixed temperature and record it each run. This converts a major uncontrolled factor (ambient temperature) into a controlled condition

Standardised mixing with replication: Fix the addition order, vessel geometry, and stirring protocol, then collect at least triplicate runs at each concentration. Replicates exposed outliers and allow proper standard errors and confidence intervals on m , n , and k .

7.3.Overall

The current dataset supports the reported orders and an average k , but its evidential strength is limited by single runs, a short concentration span, and subjective

endpoints. The three mitigations above would most directly improve reliability, and the alternative routes would offer stronger tests of the rate law with reduced bias.

8. Conclusion

The iodine clock data were described by a power-law model with fractional order in hydrogen peroxide and near-unity order in iodide. From log–log fits, the orders were $m = 0.5939$ and $n = 0.8755$; the pooled rate constant was $k = 1.113 \pm 0.091 \text{ s}^{-1} \text{ M}^{-1.47}$. The fits were linear over the tested ranges and the trial-by-trial k values were consistent, indicating that the model was adequate for prediction within these conditions.

The evidential strength was limited by single runs per condition, a narrow concentration span, subjective visual endpoints, and uncontrolled temperature. These factors likely inflated uncertainty in slopes and intercepts. The reliability of the parameters could be improved by photometric endpoint detection, thermostatted operation, and standardised mixing with replication. For OME use, the quantified rate law provides a practical basis to tune benign timing elements by concentration adjustment and to set defensible margins in design and safety documentation. Further work should obtain Arrhenius parameters for k from a temperature series and validate the orders using initial-rate methods that minimise mixing and endpoint bias.

Word Count – estimated 1050 not including Abstract, Headers, Figures, TOC, Appendix, References

9. References

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10. Appendix A – Experimental Procedure [8]

PROCEDURE

Put on the lab coat, safety goggles, and gloves. Make sure that long hair is tied.

IMPORTANT: Record all your observation sin the data sheets at the end of this script.

Lab tools and supplies:

- 50 mL conical flasks x4
- Glass pipettes x2 (pipette 1 used for KI and ascorbic acid; pipette 2 – H_2O_2) and pipette filler
- Graduated cylinder or small beaker and test tube
- Stopwatch
- Glass stirring rod

Chemicals:

Solution A (in conical flask):

- 0.20 M KI solution
- 0.010 – 0.025 M ascorbic acid (Vitamin C) solution
- 1 % starch indicator
- Distilled water

Solution B (in test tube):

- 3% H_2O_2 solution

Procedure:

I. Order of the reaction in $[H_2O_2]$

1. In four conical flasks prepare solution A according to the table. Use one glass pipette to measure the required volumes of KI and Vit C solutions. Add ~1 mL of starch solution.
2. With the second glass pipette measure the required volume of H_2O_2 (solution B) and transfer it in the test tube.
3. Pour quickly solution B from the test tube to solution A in the conical flask, stir and start the timer as soon as the solutions are mixed.
4. Record the time until the first permanent blue colour appears.

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Trial	A: KI 0.20 M (mL)	A: Vit C 0.010 M (mL)	A: Starch 1% (mL)	A: Water (mL)	B: H_2O_2 3% (mL)
I.1	3.0	1.5	1.0	18.5	1.0
I.2	3.0	1.5	1.0	17.5	2.0
I.3	3.0	1.5	1.0	16.5	3.0
I.4	3.0	1.5	1.0	15.5	4.0

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II. Order of the reaction in $[I^-]$

5. In four conical flasks prepare solution A according to the table. Use one glass pipette to measure the required volumes of KI and Vit C solutions. Add ~1 mL of starch solution.
6. With the second glass pipette measure the required volume of H_2O_2 (solution B) and transfer it in the test tube.
7. Pour quickly solution B from the test tube to solution A in conical flask, stir and start the timer as soon as the solutions are mixed.
8. Record the time until the first permanent blue colour appears.

Trial	A: KI 0.20 M (mL)	A: Vit C 0.010 M (mL)	A: Starch 1% (mL)	A: Water (mL)	B: H_2O_2 3% (mL)
II.1	1.0	1.5	1.0	18.5	3.0
II.2	2.0	1.5	1.0	17.5	3.0
II.3	3.0	1.5	1.0	16.5	3.0
II.4	4.0	1.5	1.0	15.5	3.0

11. Appendix B – Excel calculator Workbook

Part 1 (25.0 mL total): 1/t vs log₁₀([H₂O₂]₀)

[H ₂ O ₂] ₀	log ₁₀ ([H ₂ O ₂] ₀)	t (s)	1/t (s ⁻¹)	log ₁₀ (1/t)
0.0352	-1.45346	167	0.005988	-2.22272
0.0704	-1.15243	131	0.007634	-2.11727
0.1056	-0.97634	88	0.011364	-1.94448
0.1408	-0.8514	75	0.013333	-1.87506

Part 2 (25.0 mL total): 1/t vs log₁₀([I⁻]₀)

[I ⁻] ₀ (M)	log ₁₀ ([I ⁻] ₀)	t (s)	1/t (s ⁻¹)	log ₁₀ (1/t)
0.008	-2.09691	215	0.004651	-2.33244
0.016	-1.79588	142	0.007042	-2.15227
0.024	-1.61979	90	0.011111	-1.95424
0.032	-1.49485	63	0.015873	-1.79934

Figure 1: 1/t vs log₁₀([reactant]₀)

