

A Kinetic Study of Potassium Iodide with Potassium Persulfate using Iodine Clock Reaction

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Abstract

Chemical kinetics is an important area in chemistry, where the study of reaction rates is performed. Concentration of the reactants is one of the important factors that affects reaction rates. This factor can be studied by varying the concentration of the reactants in a systematic manner. An interesting aspect of kinetics is the order of a reaction. Strategies used to follow the rate of reaction depends on the type of the reaction to be followed for example, if one of the reactants or products absorbs light strongly and distinctly from the other reactants and products such type of reaction can be followed by using spectrophotometric technique. The purpose of this study was to determine the rate of the reaction of potassium iodide and potassium persulfate and to determine the order of each reactant and the overall order of the reaction as well as the activation energy of the reaction.

Keywords: Chemical kinetics; Iodine clock reaction; Arrhenius plot; Rate equations

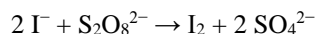
Introduction

A general equation for a chemical reaction is in the form of $aA + bB \rightarrow \text{products}$ the rate of reaction depends on several factors such as the concentration or pressure of reactants, presence or absence of a catalyst as well as temperature. The dependence of the reaction rate with the concentration of the reactants may be expressed in the form: $\text{rate} = k[A]^l[B]^m$, where k is the rate coefficient; l and m are the reaction orders with respect to the reactants A and B, respectively then the summation of $l + m$ gives the overall reaction order. Reaction orders are different from stoichiometric coefficients which are determined by calculation, the orders of the reaction are based on the kinetics of the reaction [1-3]. They are defined by the mechanism of the reaction, which is an account of the actual steps by which the molecules combine, and these orders can only be determined experimentally. However, the effect of temperature on reaction rate is given by the Arrhenius equation

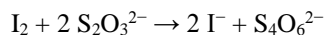
$k = Ae^{-\frac{E}{RT}}$ where A is the Arrhenius constant, E the activation energy of the reaction, R the universal gas constant and T the absolute temperature.

Several methods and strategies can be used to investigate chemical reaction kinetics and for this type of reaction, iodine clock reaction was used. I dealt with persulfate variation, this clock reaction uses sodium, potassium or ammonium persulfate to oxidize iodide ions to iodine [4,5]. Sodium thiosulfate is used to reduce iodine back to iodide before the iodine can complex with the starch to form the characteristic blue-black color [6]. These reactions are as follows

Iodine is generated



And is then removed



Methodology

Preparation of Solutions

250 cm³ of 0.2M K₂SO₄ solution was prepared as follows:

Number of moles K₂SO₄ of =CV=0.25 × 0.2=0.05 moles

Mr of K₂SO₄ = 32+2 × 39.1+16 × 4=174.2 g/mol

Mass of K₂SO₄ dissolved in 250 cm³ of distilled water=174.2 g/mol × 0.05 moles =8.71 g

250 cm³ of 0.1M K₂S₂O₈ solution was prepared as follows:

Number of moles K₂S₂O₈ of =CV=0.25 × 0.2=0.025 moles

Mr of K₂S₂O₈=(32 × 2)+39.1+16 × 8=270.2 g/mol

Mass of K₂S₂O₈ dissolved in 250 cm³ of distilled water=270.2 g/mol × 0.025 moles=6.775 g

100 cm³ of 0.2M sodium thiosulfate solution was prepared as follows:

Number of moles of sodium thiosulfate=CV=0.1 × 0.2=0.02 moles

Mr of Na₂S₂O₃=158.1 g/mol

Mass of Na₂S₂O₃ dissolved in 100 cm³ of distilled water=158.1 g/mol × 0.02 moles= 3.162 g

100 cm³ 0.2M of KNO₃ solution was prepared as follows:

Number of moles KNO₃=CV=0.1 × 0.2 moles=0.02 moles

Mr of KNO₃=101.1 g mol⁻¹

Mass of KNO₃ dissolved in 100 cm³ of distilled water=0.02 moles × 101.1 g mol⁻¹=2.022 g

The starch solution was prepared by dissolving 0.2 g of starch in 100 cm³ of warm distilled water. The preparation of reaction mixtures was done in four flasks by measuring the amounts of solutions as shown in the table below.

TABLE 1. Different reagents with different volumes that were used in the preparation of the reaction mixtures.

	# 1	# 2	# 3	# 4
Distilled water (cm ³)	10.0	10.0	10.0	10.0
0.2M Na ₂ S ₂ O ₃ (cm ³)	10.0	10.0	s10.0	10.0
Starch solution (cm ³)	5.0	5.0	5.0	5.0
0.2M KI solution (cm ³)	12.5	9.4	6.3	3.1
0.2M KNO ₃ solution (cm ³)	-	3.1	6.2	9.4

Other four empty flasks were taken and 12.5 cm³ of K₂S₂O₈ solution was added to each of them. The first flask with a reaction mixture was taken and a solution of persulfate in one the flasks was poured at the same time the reaction time was being noted for the appearance of the blue colour, the same procedure was repeated for other remaining flasks Landolt times were measured [7]. For the reaction order with respect to persulfate ion the reactions mixtures used were prepared as follows using three conical flasks labelled 5,6 and 7.

TABLE 2. Volumes of potassium persulfate and potassium sulphate that were used in the preparation of persulfate solution in test tube 5,6 and 7.

	#5	#6	#7
0.1M K ₂ S ₂ O ₈ solution (cm ³)	9.4	6.3	3.1
0.2M K ₂ SO ₄ solution (cm ³)	3.1	6.2	9.4

Also, the reaction mixture which was in tube #1 was prepared three times and reacted with #5, #6 and #7 and Landolt times were also measured. For the determination of the activation energy, the reaction mixture #1 was prepared three times again and three flasks containing 12.5 cm³ of K₂S₂O₈ solution were also prepared. One flask with the reaction mixture #1 was placed in a water bath at 30°C along together with one flask containing 12.5 cm³ of K₂S₂O₈. Another pair was placed in water bath at 35°C and the last pair in water bath at 40°C. These solutions were given enough time to equilibrate and then they were mixed together and also time was being recorded for the blue color appearance.

Results and Discussion

TABLE 3. The Landolt times for the time taken for the appearance of blue color in the reaction to appear.

Tube number	Time/s
1	139
2	202
3	330
4	658

TABLE 4. The initial concentrations of iodide and persulfate ions as well as the time taken for the blue iodine color to appear.

Tube #	[I] ₀ mol/dm ³	[S ₂ O ₈ ²⁻] ₀ mol/dm ³	Δt (s)	V ₀ Ms ⁻¹	logV ₀	log[I] ₀
1	1/15	0.025	139	2.4 × 10 ⁻⁴	-3.6	-1.2
2	0.0501	0.025	202	1.24 × 10 ⁻⁴	-3.9	-1.3
3	0.0336	0.025	330	5.1 × 10 ⁻⁵	-4.3	-1.5
4	0.0165	0.025	658	1.25 × 10 ⁻⁵	-4.9	-1.8

TABLE 5. Landolt times for the time taken for the appearance of a blue color in the reaction to appear.

Test tube number	Time/s
5	205
6	288
7	598

TABLE 6. Initial concentrations of iodide and persulfate ions as well as the time taken for the blue iodine color to appear.

Tube #	[S ₂ O ₈ ²⁻] ₀ mol/dm ³	[I] ₀ mol/dm ³	Δt (s)	V ₀ Ms ⁻¹	logV ₀	log[S ₂ O ₈ ²⁻] ₀
5	0.0752	0.05	205	3.7 × 10 ⁻⁴	-3.4	-1.1
6	0.0504	0.05	288	1.75 × 10 ⁻⁴	-3.8	-1.3
7	0.0248	0.05	598	4.1 × 10 ⁻⁵	-4.4	-1.6

TABLE 7. Landolt times for the time taken for the appearance of the blue color when the reaction mixtures were at different temperatures.

Temperature/°C	30	35	40
Time /s	101	72	65

TABLE 8. Shows the initial concentration of persulfate ion and the time taken for the blue colour of iodine formation when the reaction mixtures were at different 30, 35 and 40°C.

[S ₂ O ₈ ²⁻] ₀ mol/dm ³	Temperature/K	Δt/s	V ₀ Ms ⁻¹	lnV ₀	1/T
0.025	303.15	101	2.5 × 10 ⁻⁴	-8.3	0.0033
0.025	308.15	72	3.5 × 10 ⁻⁴	-8.0	0.0032
0.025	313.15	65	4.0 × 10 ⁻⁴	-7.8	0.0031

Determination of the reaction order with respect to iodide concentration: refer to TABLE 4

The initial concentration of the iodide ion [I]₀ in the reaction mixture of tube #1 is given by

$$C_1V_1=C_2V_2$$

$$0.2 \times 12.5 = C_2 \times 37.5$$

$$C_2 = \frac{I}{15} M \text{ and the initial reaction rate is given by } \frac{[I-]_0}{2\Delta t} = \frac{I}{15 \times 2} M \div 139s = 2.4 \times 10^{-4} Ms^{-1}$$

The initial concentration of the iodide ion [I]₀ in the reaction mixture of tube #2 is given by

$$C_1V_1=C_2V_2$$

$$0.2 \times 9.4 = C_2 \times 37.5$$

$$C_2 = 0.0501 M \text{ and the initial reaction rate is given by } \frac{0.0501M}{(2 \times 202s)} = 1.24 \times 10^{-4} Ms^{-1}$$

The initial concentration of the iodide ion $[I^-]_0$ in the reaction mixture of tube #3 is given by

$$C_1V_1 = C_2V_2$$

$$0.2 \times 6.3 = C_2 \times 37.5$$

$$C_2 = 0.0336 \text{ M and the initial reaction rate is given by } \frac{0.0336M}{(2 \times 330s)} = 5.1 \times 10^{-5} \text{ Ms}^{-1}$$

The initial concentration of the iodide ion $[I^-]_0$ in the reaction mixture of tube #4 is given by

$$C_1V_1 = C_2V_2$$

$$0.2 \times 3.1 = C_2 \times 37.5$$

$$C_2 = 0.0165 \text{ M and the initial reaction rate is given by } \frac{0.0165M}{(2 \times 658s)} = 1.25 \times 10^{-5} \text{ M / s}$$

The initial concentration of persulfate ion $[S_2O_8^{2-}]_0$ in all four flasks with reaction mixtures given by

$$C_1V_1 = C_2V_2$$

$$0.1 \times 12.5 = C_2 \times 50$$

$$C_2 = 0.025 \text{ M}$$

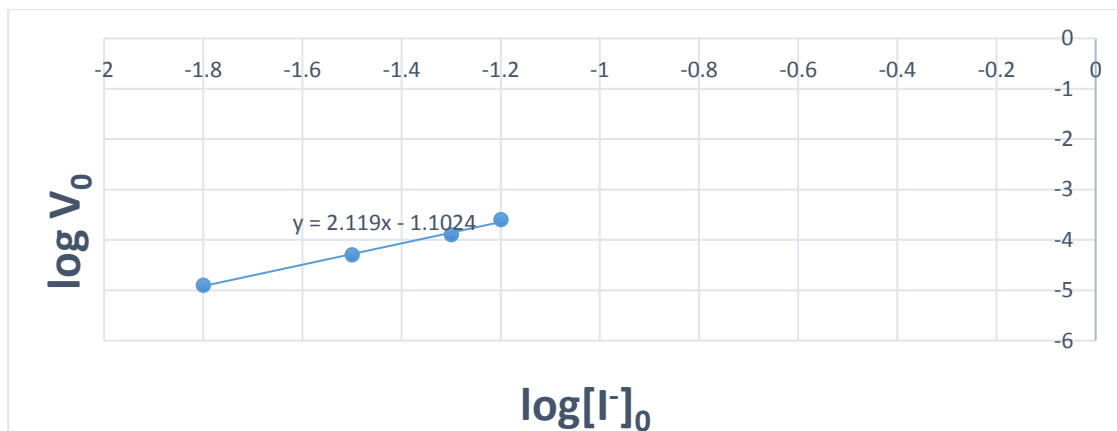


FIG. 1. A graph of $\log V_0$ vs $\log [I^-]_0$

Using equation in the form: $\text{rate}_1 = k [I^-]^n [S_2O_8^{2-}]^m$

Substituting values in table 4 and 6 highlighted in blue and green for test tube number 7 and number 4 gives

$$\frac{4.1 \times 10^{-5}}{1.25 \times 10^{-5}} = \frac{k \times 0.05^n \times 0.025^m}{k \times 0.0165^n \times 0.025^m}$$

$$n = \log \frac{\frac{4.1 \times 10^{-5}}{1.25 \times 10^{-5}}}{\frac{0.05}{0.0165}} = 1.07 \approx 1$$

therefore, the reaction order n with respect to iodine ion=1

Determination of reaction order with respect to persulfate concentration [TABLE 6]

The initial concentration of persulfate $[S_2O_8^{2-}]_0$ ion in the reaction mixture of tube #5 is given by

$$C_1V_1 = C_2V_2$$

$$0.1 \times 9.4 = C_2 \times 12.5$$

$$C_2 = 0.0752M \text{ and the initial reaction rate is given by } \frac{[S_2O_8^{2-}]}{\Delta t} = \frac{0.0752M}{205s} = 3.7 \times 10^{-4} Ms^{-1}$$

The initial concentration of persulfate $[S_2O_8^{2-}]_0$ ion in the reaction mixture of tube #6 is given by

$$C_1 V_1 = C_2 V_2$$

$$0.1 \times 6.3 = C_2 \times 12.5$$

$$C_2 = 0.0504M \text{ and the initial reaction rate is given by } \frac{[S_2O_8^{2-}]}{\Delta t} = \frac{0.0504M}{288s} = 1.75 \times 10^{-4} Ms^{-1}$$

The initial concentration of persulfate $[S_2O_8^{2-}]_0$ ion in the reaction mixture of tube #7 is given by

$$C_1 V_1 = C_2 V_2$$

$$0.1 \times 3.1 = C_2 \times 12.5$$

$$C_2 = 0.0248M \text{ and the initial reaction rate is given by } \frac{[S_2O_8^{2-}]}{\Delta t} = \frac{0.0248M}{598s} = 4.1 \times 10^{-5} Ms^{-1}$$

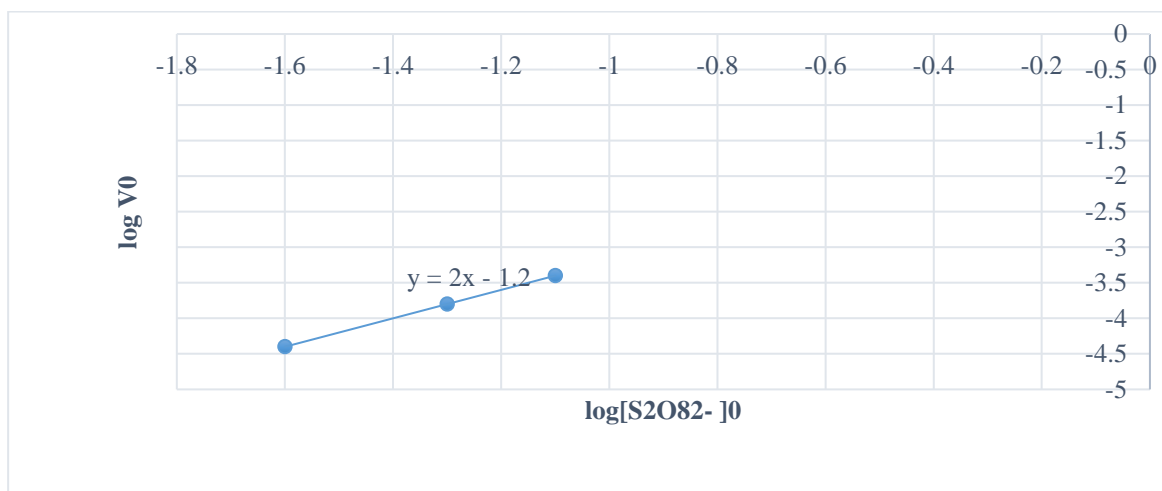


FIG 2. A graph of $\log V_0$ vs $\log[S_2O_8^{2-}]_0$.

Substituting values in TABLE 4 and 6 highlighted in blue and green for test tube number 5 and number 2 gives

$$\frac{3.7 \times 10^{-4}}{1.24 \times 10^{-4}} = \frac{k \times 0.05^n \times 0.0752^m}{k \times 0.05^n \times 0.025^m}$$

$$m = \log \frac{3.7 \times 10^{-4}}{1.24 \times 10^{-4}} = 0.99 \approx 1$$

Therefore, the reaction order m with respect to persulfate ion=1

Determination of the activation energy: refer to table 8

The initial concentration of persulfate ion, $[S_2O_8^{2-}]_0$ in the reaction mixture after mixing with contents of tube #1 at 30°C is calculated as follows

$$C_1V_1=C_2V_2$$

$$0.1 \times 12.5 = C_2 \times 50$$

$$= 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

The initial concentration of persulfate ion, $[S_2O_8^{2-}]_0$ in the reaction mixture after mixing with contents of tube #1 at 35°C is calculated as follows:

$$C_1V_1=C_2V_2$$

$$0.1 \times 12.5 = C_2 \times 50$$

$$C_2 = 0.025\text{M and the initial reaction rate at 35°C is given by } \frac{[S_2O_8^{2-}]}{\Delta t} = \frac{0.0252\text{M}}{72\text{s}} = 3.5 \times 10^{-4} \text{ Ms}^{-1}$$

The initial concentration of persulfate ion, $[S_2O_8^{2-}]_0$ in the reaction mixture after mixing with contents of tube #1 at 40°C is calculated as follows:

$$C_1V_1=C_2V_2$$

$$0.1 \times 12.5 = C_2 \times 50$$

$$C_2 = 0.025\text{M and the initial reaction rate at 40°C is given by } \frac{[S_2O_8^{2-}]}{\Delta t} = \frac{0.025\text{M}}{65\text{s}} = 4.0 \times 10^{-4} \text{ Ms}^{-1}$$

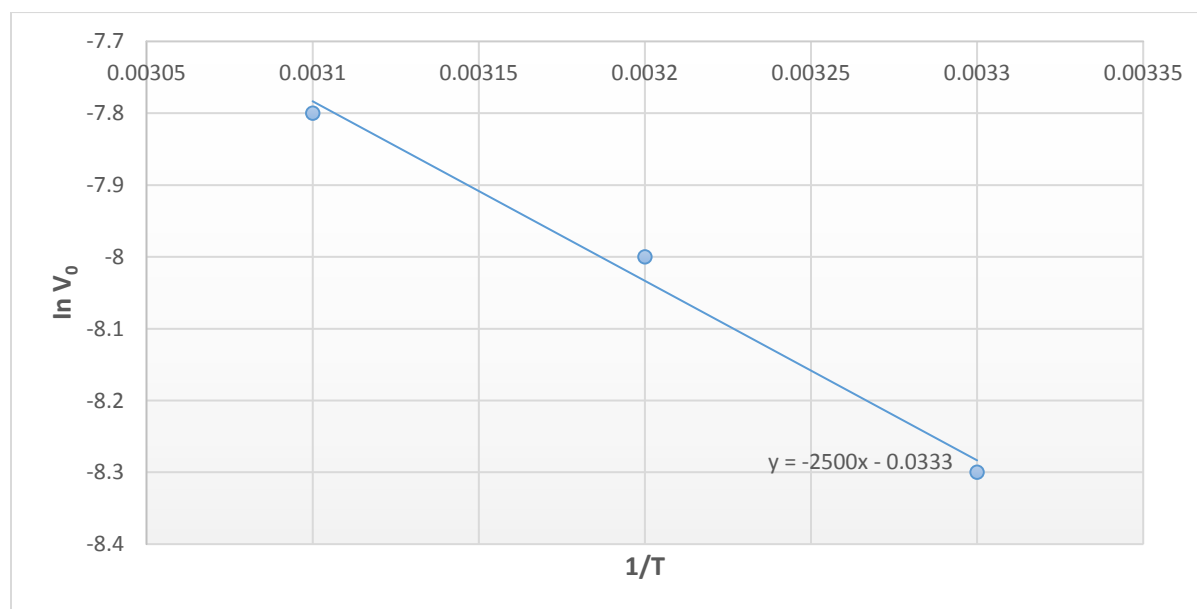


FIG 3. Graph of $\ln V_0$ vs $1/T$.

From the plot of $\ln V_0$ versus $1/T$ slope is the activation energy and is calculated as follows:

$$\text{Gradient} = -2500 \text{ K}$$

$$\text{but slope} = -\frac{E_a}{R} \text{ therefore}$$

$$-2500K = -\frac{E_a}{R}$$

$$E_a = 2500 K \times 8.3144 \text{ Jmol}^{-1} \text{ K}^{-1} = 20786 \text{ Jmol}^{-1}$$

$$E_a = 20.786 \text{ KJ/mol}$$

From this study I found the reaction order with respect to iodide ion to be 1 and also the reaction order with respect to persulfate ion was found to be 1 as well. Comparing these values to the literature ones, they seem to agree in most cases. In chemistry we define activation energy as the minimum amount of energy reactants must have in order to start a reaction in this study I also determined this energy by varying the temperature and measuring the rate of reactions then, I used them to construct an Arrhenius plot and solve for E_a where this value was obtained from the slope. I found the activation energy of the reaction to be 20.7 KJ/mol but the theoretical value is reported to be somewhere around 30 KJ/mol, the reason for this deviation can be accounted for by saying this was as a result of removing the test tube containing persulfate ion from the water bath during mixing so when it was mixed with the contents of tube 1 the this test tube was no longer at the same temperature as it was in a water bath. A logarithmic plot of the reaction rate against concentration shows a linear relationship in both cases with a positive gradient which shows that the rate of reaction increases with increasing concentration. This actually make sense because there will be greater chance for molecules to collide and speed up the reaction rate.

Conclusion

For this study, I utilized the iodine clock reaction between iodide ion and persulfate ion to determine the order of reaction with respect to iodide ion and persulfate ion and it was found to be 1, which is reported in most literatures. I also determined the activation for the reaction and it was found to be 20 KJ/mol.

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