

NOTE

KINETICS OF THE OXIDATION OF VITAMIN C

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Received April 9, 2012; Accepted October 31, 2012

ABSTRACT

Vitamin C or ascorbic acid is needed by the human body but it is already damaged by the rise in temperature due to be oxidized to L-dehydroascorbic acid. This research aims to determine the kinetics of oxidation of ascorbic acid due to an increase of temperature (40-80 °C) and to design an ascorbic acid oxidation reaction laboratory module to be applied in the senior high school reaction kinetics curriculum. The determination of the kinetics of the oxidation of ascorbic acid applies the integral and half-change time methods, while the concentration of the remained ascorbic acid in sixty minute intervals is determined by iodimetric titration method. Decomposition of ascorbic acid was measured at 40, 50, 60, 70 and 80 °C. The results of this research indicate that at 40, 50, 60, 70 and 80 °C the kinetics of the oxidation of ascorbic acid is a first-order reaction with rate constants of 4.55×10^{-4} , 5.85×10^{-4} , 8.4×10^{-4} , 1.1×10^{-3} and $1.015 \times 10^{-3} \text{ min}^{-1}$, respectively. Pre-exponential factor or the frequency of collisions is a factor which is a measure of the collision rate. The activation energy and the pre-exponential factor for the oxidation of ascorbic acid were found to be $20.73 \text{ kJ.mol}^{-1}$ and 1.372 min^{-1} . The procedure used in this study was modified into a laboratory module will be applied in the teaching of reaction kinetics at the senior high school level.

Keywords: ascorbic acid; kinetic reaction; temperature

ABSTRAK

Vitamin C atau asam askorbat sangat dibutuhkan oleh tubuh manusia tetapi sangat mudah rusak oleh kenaikan temperatur karena teroksidasi menjadi asam L-dehidroaskorbat. Penelitian ini bertujuan untuk menentukan kinetika reaksi oksidasi vitamin C pada temperatur 40-80 °C serta merancang eksperimen kinetika reaksi oksidasi vitamin C yang dapat dilakukan di tingkat sekolah menengah atas. Penentuan kinetika reaksi oksidasi vitamin C dilakukan dengan menggunakan metode integral dan grafik sedangkan kadar asam askorbat sisa ditentukan dengan metode titrasi iodimetri tiap interval waktu enam puluh menit. Kerusakan vitamin C diukur pada temperatur 40, 50, 60, 70 dan 80 °C. Hasil penelitian menunjukkan bahwa kinetika reaksi oksidasi vitamin C mengikuti reaksi orde satu pada temperatur 40, 50, 60, 70 dan 80 °C dengan tetapan laju reaksi berturut-turut $4,55 \times 10^{-4}$, $5,85 \times 10^{-4}$, $8,4 \times 10^{-4}$, $1,1 \times 10^{-3}$ dan $1,015 \times 10^{-3} \text{ menit}^{-1}$. Energi aktivasi dan faktor pre-eksponensial reaksi oksidasi asam askorbat adalah $20,73 \text{ kJ.mol}^{-1}$ dan $1,372 \text{ menit}^{-1}$. Faktor pre-eksponensial atau frekuensi tumbukan adalah faktor yang merupakan ukuran laju terjadinya tumbukan. Prosedur yang digunakan dalam penelitian ini dimodifikasi ke dalam modul laboratorium untuk diterapkan dalam pengajaran kinetika reaksi pada tingkat SMA

Kata Kunci: Vitamin C; kinetika reaksi; temperatur

INTRODUCTION

Vitamins are a group of organic complex compounds that the body needs in small quantities. Vitamins must be supplied from outside, as the human body cannot synthesize them. One such vitamin is Vitamin C. The exact amount of Vitamin C that the body needs is unknown, and is thought to be anywhere from 45 to 75 mg a day [1].

Vitamin C, or ascorbic acid, is a vitamin that can be found in various fruits and vegetable. Vitamin C is a white, crystal-shaped organic compound, and can be synthesized from glucose or extracted from certain natural sources such as orange juice. The vitamin was first isolated from lime juice by Szent Gyorgy in 1928 [2].

Vitamin C plays a vital role in our lives; Firstly, it contributes in to the synthesis of collagen tissue around

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bones, teeth, cartilage, skin, and damaged tissue. Second, this vitamin is needed to activate various enzymes related to the nervous system, hormones, and detoxification of medicine and poison in the liver. Third, its role as an antioxidant is well-known in society; its solubility enables it to work as antioxidant within our bodily fluids. Fourth, Vitamin C increases the rate of absorption of iron, calcium, and folic acid. Fifth, it reduces allergic reactions, boosts the immune system, stimulates the formation of bile in the gallbladder, and facilitates the excretion of various steroids [3]. Vitamin C is important in the functioning of the brain, as the brain contains a large amount of Vitamin C. A study by two researchers at the Texas Woman's University found that high school students with high blood Vitamin C rates produced better IQ test compared to students with low rates.

Fruits and vegetables, like oranges, greens, tomatoes, potatoes, and berries are the main source of Vitamin C for humans.

Vitamin C is highly soluble in water and alcohol, and is easily oxidized. The oxidation of Vitamin C occurs very quickly in a base environment at high temperatures. "Light and heat damage Vitamins B and C in fruits and vegetables. Vitamin B and C also decreases if food is left warm or hot for too long" [4]. This is often inevitable in the processing of food that contains Vitamin C such as fruits and vegetables.

The important role of Vitamin C in metabolism has resulted in a plethora of research, among others: The determination of the amount of Vitamin C in various drinks using the redox titration method. This method produces accurate results, despite the low levels of ascorbic acid present [5]. The determination of the amount of Vitamin C in various fruits and vegetables also can be done by bipotentiometric iodimetric titration method. This method produces efficient ascorbic acid quantification at relatively low prices with cheap equipment [6]. Comparisons between the iodimetric and visible spectrophotometric methods of Vitamin C determination show that spectrophotometry is less viable, as it is more expensive and time-consuming than iodimetry with insignificant differences in accuracy [7]. The effect of storage at room temperature on the amount of Vitamin C, show that the amounts is significantly reduced if it is stored at room temperature [8]. Vitamin C levels decrease significantly at room temperature it is necessary to determine the kinetics of the oxidation of vitamin C.

Based on the above results, the authors were interested to further study the effect of heating, at various temperatures, on the kinetics of the oxidation of Vitamin C, using iodimetric titration method in determining the amount of Vitamin C present.

EXPERIMENTAL SECTION

Materials

Materials used in this study were Vitamin C p.a, 0.01 N Iodine solution, KI, 1% starch solution, and deionized water.

Instrumentation

Equipments used in this study, were Erlenmeyer, measuring glass, chemical glass, Petridish, measuring flask, stirring rod, analytic scale, burette, funnel, volume pipette, pipette, stand and clamp, oven, timekeeper, and spray bottle.

Procedure

Provision of material

Solutions used in this study, among others were 0.01 N Iodine solution, 1% starch solution.

The 0.01 N Iodine solution was made by adding 23 g of KI to 1.27 g of powdered Iodine, dissolving it in 25 mL of deionized water, and transporting it into a 1000 mL measuring flask before adding deionized water up to the mark [9-10].

The 1% starch solution was made by dissolving 1 g of starch in 100 mL of hot water. This solution was used as the indicator.

Determination of the oxidation reaction kinetics of vitamin C

Ascorbic acid 0.5 g dissolved with deionized water in a 100 mL measuring flask. 6 cleaned Erlenmeyer are then taken and labeled from A to F. Each Erlenmeyer is filled with 5 mL of ascorbic acid. Vitamin C in Erlenmeyer B, C, D, E, and F are heated at 40 °C in 60 min increments (60 min for Erlenmeyer B, 120 min for Erlenmeyer C, 180 min for Erlenmeyer D, 240 min for Erlenmeyer E, and 300 min for Erlenmeyer F). This is followed by the determination of Vitamin C rates in each sample (Erlenmeyer A, B, C, D, E, and F) through the titration of 5 mL of Vitamin C solution with a Iodine 0.01 N solution, and a 1% Starch solution as the indicator, Blue indicates the end of the titration.

This method is repeated at various temperatures 50, 60, 70, and 80 °C and ascorbic acid concentrations.

Data analysis

Determination of vitamin C rates. Vitamin C oxidation rates can be determined through the titration of an I₂ 0.01 N solution with a 1 mL starch indicator. 1 mL I₂ solution 0.01 N = 0.88 mg Vitamin C [10].

Table 1. Ascorbic acid percentages at time t for T = 40, 50, 60, 70, and 80 °C

Temperature (°C)	Ascorbic acid first concentration (M)	% ascorbic acid left in heating process for (min)					
		0	60	120	180	240	300
40	0.0142	100	97.535	94.718	92.254	89.437	87.324
	0.0284	100	97.432	94.267	92.156	89.694	87.056
50	0.0142	100	95.774	91.549	88.028	85.916	83.451
	0.0284	100	95.599	91.373	87.676	85.035	83.099
60	0.0142	100	95.070	90.845	86.972	83.451	80.282
	0.0284	100	92.606	90.141	86.796	82.746	79.578
70	0.0142	100	90.845	87.324	83.099	81.690	78.873
	0.0284	100	90.141	86.972	84.507	81.338	78.521
80	0.0142	100	95.422	86.620	82.394	78.873	77.113
	0.0284	100	93.662	86.268	82.042	77.993	75.704

Determination of reaction order and reaction rate constant. The kinetics of the oxidation reaction of Vitamin C which covers its reaction order, reaction rate constant, and activation energy are determined through observation. The half-time method is used to determine the reaction's order and reaction rate constant. The half-time method uses Equations 1, 2, and 3. The activation energy is determined through Equation 4.

$$\frac{\left(\frac{1}{t}\right)_1}{\left(\frac{1}{t}\right)_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \quad (1)$$

$$\frac{t_{x\%}}{t_{50\%}} = \frac{1}{k} \left(\ln \frac{[A_0]}{[A_x]} \right) \quad \text{for first reaction order} \quad (2)$$

$$\frac{t_{x\%}}{t_{50\%}} = \frac{1}{k} \left(\frac{1}{[A_x]} - \frac{1}{[A_0]} \right) \quad \text{for second reaction order} \quad (3)$$

$$\ln k = \left(-\frac{E_a}{R} \right) \left(\frac{1}{T} \right) + \ln A \quad (4)$$

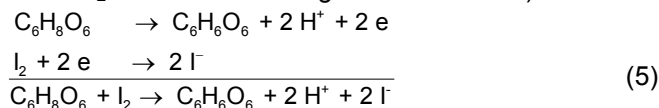
$$y = m x + b$$

RESULT AND DISCUSSION

The Iodimetric Titration method by direct titration with a standard Iodine solution was used to determine Vitamin C oxidation reaction kinetics. This method is effective as Vitamin C is easily oxidized and Iodine is easily reduced. To avoid the dissipation of Iodine through evaporation, Iodine is reacted with KI to form Tri-iodide ions (I_3^-), rendering iodine dissipation negligible (with at least 4% KI) [9]. The standardization of the iodine solution is unnecessary; as the water content in ascorbic acid is very low, the error produced is still within the tolerance limits of the titration method [11].

If in the acidic solution containing both Vitamin C and carbohydrates (from starch as an indicator) are

added with Iodine, Vitamin C oxidized, the Iodine is reduced, than the solution turns to purple. This color change is the basis will be of the titration reaction, and the purple indicates the end of the reaction process [12]. From this titration the amount (in mL) of iodine solution used, is obtained which is equivalent to the concentration of the ascorbic acid remained in each 60 min interval sample (Erlenmeyer A to F). (1 mL of 0.01 N I_2 solution = 0.88 mg of ascorbic acid)



As each ascorbic acid molecule loses 2 electrons through titration, its equivalent weight is half of it's the molecular weight, 88.07 g/ek.

This study has determined the concentration of ascorbic acid at various temperatures (40, 50, 60, 70, and 80 °C) in 60 min intervals. The concentrations of ascorbic acid can then be used to determine the reaction order and reaction rate constant of the oxidation reaction of ascorbic acid at various temperatures.

Determination of the Reaction Velocity Constant and Reaction Order of the Oxidation Reaction of Ascorbic Acid

Table 1 shows the results of determination of the reaction rate constant and order of Vitamin C oxidation at 40, 50, 60, 70, and 80 °C.

Based on this data, the reaction rate constant and order can be determined with the half-time method; the various initial-remain ascorbic acid percentage values, with time intervals t substituted into Equations 2 and 3. These calculations can be found in Table 2.

From Table 2 it can be seen that the data for the initial concentrations of both 0.0412 M and 0.0284 M ascorbic acid tend to be constant; therefore half-time is independent on initial concentration and initial value. Based on Table 2, the half-time is between

Table 2. Half-time at various temperatures and time intervals for a first order reaction

Temperature (°C)	Ascorbic acid first concentration (M)	Acid Half-time at each time interval of t				
		60	120	180	240	300
40	0.0142	1666.1	1532.5	1547.1	1489.8	1533.8
	0.0284	1598.5	1408.5	1527.1	1529.1	1499.8
50	0.0142	963.1	941.9	978.3	1095.6	1149.2
	0.0284	923.8	921.8	948.4	1026.0	1122.9
60	0.0142	822.5	866.1	893.6	919.3	946.6
	0.0284	541.3	801.2	880.9	878.2	910.1
70	0.0142	433.1	613.5	673.8	822.4	876.0
	0.0284	400.6	595.8	741.0	805.2	859.8
80	0.0142	887.4	578.9	644.1	700.8	799.9
	0.0284	635.0	563.0	630.2	669.2	746.9

Table 3. Reaction order calculation based on the half-time method at 40 °C

Time (t)	Reaction Order (n) at temperature of 40 °C				
	40 °C	50 °C	60 °C	70 °C	80 °C
60	1.060	1.060	1.603	1.112	1.483
120	1.122	1.031	1.112	1.042	1.040
180	1.019	1.045	1.021	0.863	1.031
240	0.962	1.095	1.066	1.030	1.067
300	1.032	1.033	1.057	1.027	1.099

Table 4. Velocity constant of the oxidation reaction of ascorbic acid at various temperatures and time intervals

No.	t (min)	The value of reaction rate constant, k (min^{-1}) at temperature of				
		40 °C	50 °C	60 °C	70 °C	80 °C
1	60	0.00043	0.00060	0.00106	0.00167	0.00094
2	120	0.00047	0.00063	0.00083	0.00115	0.00122
3	180	0.00045	0.00059	0.00079	0.00099	0.00107
4	240	0.00046	0.00057	0.00077	0.00085	0.00096
5	300	0.00046	0.00054	0.00075	0.00080	0.00090
	average	0.00045	0.00059	0.00084	0.00109	0.00102

650-1500 min; much longer than the data gathered 300 min. Thereafter, the integration method was used to obtain the reaction's order, and it was found that on the 0th, 1st, and 2nd orders the reaction's rate constant tended to be constant, and the regression coefficient tended to be linear. Hence, the integration method has failed to find the reaction's order with a total combined time of 300 min. The alternative we uses the half-time method to determine the oxidation reaction of ascorbic acid's reaction order. The results of are shown in Table 3, based upon data from Table 2 and by using Equation 1.

Data from Table 3 shows a first order reaction. Hence, the oxidation reaction of ascorbic acid is a first order reaction. This result is consistent with previous research: 1) Research investigating ascorbic acid degradation kinetics, using titration with 2,6-dichlorophenol indophenol, suggests a first order reaction for temperatures between 4 and 5 °C [13]. 2) Vitamin C degradation determined using the potentiometric method at 37.8 and 46.1 °C also suggests a first order reaction [14]. 3) Vitamin C degradation kinetics in storage at temperatures between 25 and 45 °C in 5 °C intervals, respectively, with Vitamin C

concentration determined through titration with 2,6-dichlorophenol, suggests a first order reaction [15].

By entering data from Table 1 into the first order reaction velocity equation, the value of the reaction velocity constant can be determined:

$$kt = \ln \frac{a}{(a-x)} \quad (6)$$

where a is the (percent) initial concentration of ascorbic acid and $(a-x)$ the (percent) ascorbic acid remaining after each time interval. The calculations results are shown in Table 4.

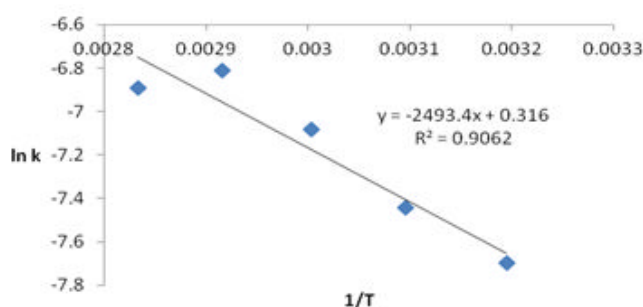
Based on these calculations, the rate constants at 40, 50, 60, 70, and 80 °C are 0.00045, 0.00059, 0.00084, 0.00109, and 0.00102 unit respectively.

Activation Energy and Pre-exponential Factor Determination

The reaction rate constant data from Table 4 shows that the rate constant (k) rises with temperature. This is consistent with the Arrhenius Theory. Increase in temperature also increases the kinetic energy of the substance. The activation energy of the oxidation reaction of Vitamin C can be determined based on data

Table 5. Basic Competence, Learning Activities, and Indicators of reaction kinetics study in high school

Basic Competence	Learning Activities	Indicators
Describing and understanding reaction rate through an experiment investigating the factors that influence reaction rate.	<ul style="list-style-type: none"> Calculating and making a solution of a specific concentration in groups, in the laboratory. Designing and conducting an experiment to investigate the factors that influence reaction rate, in the laboratory Concluding the factors that determine reaction rate. 	<ul style="list-style-type: none"> Calculating the concentration of a solution (solution molarity) Analyzing the factors that influence reaction rate (concentration, surface area, temperature, and catalysts) through experimentation. Plotting a graph from experimental data regarding the factors that influence reaction rate.

**Fig 1.** The relation between $\ln k$ and $1/T$ in the oxidation reaction of ascorbic acid

from Table 4 and using Equation 4. Plotting $\ln k$ against $\frac{1}{T}$ gives Fig. 1.

Fig. 1 shows the regression equation $y = 0.316 - 2493x$ with $R^2 = 0.906$. Based on the regression equation, pre-exponential factor of 1.372 min^{-1} and activation energy of $20.726 \text{ kJ.mol}^{-1}$ can be obtained.

$$\ln k = \left(-\frac{E_a}{R} \right) \frac{1}{T} + \ln A$$

$$y = mx + b \quad -\frac{E_a}{R} = -2493$$

$$y = -2493x + 0.316 \quad E_a = 2493 \text{ K} \times 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$$

$$\ln A = 0.316 \quad = 20726.8 \text{ J.mol}^{-1}$$

$$A = 1.372 \quad = 20.73 \text{ kJ.mol}^{-1}$$

So the relation of reaction rate constant and activation energy for Vitamin C oxidation reaction can be written as:

$$k = 13.32 e^{\frac{20.73}{RT}} \quad (7)$$

Activation energy of vitamin C oxidation reaction of $20.73 \text{ kJ.mol}^{-1}$ shows that reaction rate constant changes with energy of $20.73 \text{ kJ.mol}^{-1}$ towards the temperature. Pre-exponential factor of 1.372 min^{-1} means that the rate of the collision of $20.73 \text{ kJ.mol}^{-1}$ or collision factor that has energy of $20.73 \text{ kJ.mol}^{-1}$ that can produce reaction is 1.372 min^{-1} .

Designing a Reaction Kinetics Lab Module for High School

Reaction Kinetics is taught on first semester of the second year of high school with previous knowledge of reaction kinetics, chemical balance and the factors that influence it, and its application in everyday life and industry. It is allocated 4 teaching hours, with basic competence and indicators to be fulfilled displayed in Table 5.

Learning material and some reaction kinetics core modules have been designed based on Table 5. Specifically, the lab module has been designed to include the creation of an ascorbic acid solution at varying concentrations, the effects of concentration and temperature on the reaction rate of the oxidation reaction of ascorbic acid, and the plotting of experimental data on a graph.

CONCLUSION

The result of the research shows that oxidation reaction kinetic of vitamin C follows the first order reaction at temperature of 40, 50, 60, 70 and 80 °C with values of reaction rate constant respectively 4.55×10^{-4} , 5.85×10^{-4} , 8.4×10^{-4} , 1.1×10^{-3} , $1.015 \times 10^{-3} \text{ min}^{-1}$ with activation energy of $20.73 \text{ kJ.mol}^{-1}$, pre-exponential factor 1.372 min^{-1} . Study the module that has been made is referring to curriculum of chemistry KTSP (curriculum level of set of education) 2006 which is now used in high schools, thus it's expected to be able to help the teachers in chemical reaction kinetic study. For the next research, it is suggested for oxidation reaction kinetic of Vitamin C determination in fruits and vegetables using another method, for example "Clock Reaction" method and also with longer time interval. Designing the determination of reaction kinetic using computer should be used in high school.

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