KINETICS OF THE OXIDATION OF VITAMIN C

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ABSTRACT

Vitamin C or ascorbic acid is necessary for the human body, although only in small quantities. Ascorbic acid is acquired through food, as the human body cannot synthesize ascorbic acid. Vitamin C is a kind of vitamin that can be found in fruit and vegetables. There are many advantages we can find in vitamin C. First, vitamin C helps and preserves colagen structure. Second, vitamin C has a role as antioxidant. Third, vitamin C is needed for activation of various enzym. Fourth, vitamin C can increase the absorption of ferum, calcium, and folat acid. Vitamin C is very easily decomposed by increases in temperature, ascorbic acid will be oxidized to become L-dehydroaskorbat acid. This is hard to prevent in foodstuff processing of which contains vitamin C, such as vegetables and fruits. This research aims to determine the kinetics of oxidation of ascorbic acid due to an increase in temperature (40^0C – 80^0C) and to create 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 remaining ascorbic acid in sixty minute intervals is determined by iodimetric titration method. Decomposition of ascorbic acid is measured at 40^0C, 50^0C, 60^0C, 70^0C and 80^0C. The results of this research indicate that at 40^0C, 50^0C, 60^0C, 70^0C and 80^0C the kinetics of the oxidation of ascorbic acid is a first-order reaction with a rate constants of 4.55×10^{-4} minute^{-1}, 5.85×10^{-4} minute^{-1}, 8.4×10^{-4} minute^{-1}, 1.1×10^{-3} minute^{-1} and 1.015×10^{-3} minute^{-1}, respectively. The activation energy and the pre-exponential factor for the oxidation of ascorbic acid were found to be 20.73 kJ. mol^{-1} and 1.372 minute^{-1}. The procedure used in this study was modified into a laboratory module to be applied in the teaching of reaction kinetics at the senior high school level.

Keyword : *ascorbic acid, kinetic reaction, temperature*

INTRODUCTION

Vitamins are a group of organic complex compounds that the body needs in small quantities. Vitamins must be supplies from outside, as the human body cannot synthesize them. One such vitamin is Vitamin C. The exact amount of Vitamin C 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 to the synthesis of collagen tissue around 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 to 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 results as 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. The only source of animal protein is milk and liver.

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 to 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 using the 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 spectrophotomeric 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 versus refrigeration on the amount of Vitamin C. Results show that Vitamin C amounts are significantly reduced if stored at room temperature.[8]

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 reaction of Vitamin C, using the iodimetric titration method in determining the amount of Vitamin C present.

II. METHODOLOGY

II.1 Location and Time of Research

This study was conducted at the Material Physics Chemistry Laboratory, of the F-MIPA study program of the Bandung Institute of Technology. The preparatory stage was launched in February. Research began in June 2008 and ended in October 2008.

EQUIPMENT AND MATERIAL USED

Equipment used in this study: 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.

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

PROCEDURE AND DATA ANALYSIS

Provision of Material

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

The 0.01 N Iodine solution was made by adding 23 grams of KI to 1.27 grams 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 gram of starch in 100 mL of hot water. This solution was used as the indicator.

Determination of the Oxidation Reaction Kinetics of Vitamin C

0.5 grams of ascorbic acid is weighed and dissolved with deionized water in a 100 mL measuring flask. 6 cleaned Erlenmeyers are then taken and labelled from A to F. Each Erlenmeyer is filled with 5 mL of ascorbic acid. Vitamin C in Erlenmeyers B, C, D, E, and F are heated at 40^0C in sixty minute increments (60 minutes for Erlenmeyer B, 120 minutes for Erlenmeyer C, 180 minutes for Erlenmeyer D, 240 minutes for Erlenmeyer E, and 300 minutes for Erlenmeyer F). This is followed by the determination of Vitamin C rates in each sample (Erlenmeyers A, B, C, D, E, and F) through the titration of 5 mL of Vitamin C solution with a Iodium 0.01 N solution, with a 1% Starch solution as the indicator, blue indicating the end of the titration.

This method is repeated at various temperatures 50, 60, 60, and 80 degrees Celsius and ascorbic acid concentrations.

DATA ANALYSIS

Determination of Vitamin C Rates

Vitamin C rates can be determined through the titration of a I2 0.01 N solution with a 1 mL starch indicator. 1 mL I_2 solution 0.01 N = 0.88 mg Vitamin C. [10]

Determination of Reaction Order and Reaction Velocity Constant

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

$$\frac{(t_{\frac{1}{2}})_1}{(t_{\frac{1}{2}})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \qquad \text{(II.1)}$$

$$\frac{t_{x\%}}{t_{50\%}} = \frac{\frac{1}{k}\left(\ln\frac{[A_0]}{[A_x]}\right)}{\frac{1}{k}\left(\ln\frac{100}{50}\right)}$$ For first reaction order (II.2)

$$\frac{t_{x\%}}{t_{50\%}} = \frac{\frac{1}{k}\left(\frac{1}{[A_x]}-\frac{1}{[A_0]}\right)}{\frac{1}{k}\left(\frac{1}{50}-\frac{1}{100}\right)}$$ For second reaction order (II.3)

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$
$$y = m \quad x + b \qquad \text{(II.4)}$$

RESULTS AND ANALYSES

The Iodimetric Titration method was used to determine Vitamin C oxidation reaction kinetics; direct titration with a standard Iodine solution. 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 into an acidic solution containing both Vitamin C and carbohydrates (using starch as an indicator) we add Iodine, Vitamin C oxidises, Iodine subsists, and the solution turns purple. This color change is the basis of the titration reaction, and purple indicates the end of the reaction process.[12] From this titration we obtain the amount (in mL) of iodine solution used, which is equivalent to the concentration of the remainder ascorbic acid in each 60 minute interval sample (Erlenmeyers A to F). (1 mL of 0.01 N I_2 solution = 0.88 mg of ascorbic acid)

$$C_6H_8O_6 \longrightarrow C_6H_6O_6 + 2\,H^+ + 2\,e$$
$$I_2 + 2\,e \longrightarrow 2\,I^- \qquad \text{(III.1)}$$
$$C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2\,H^+ + 2\,I^-$$

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

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

III.1 Determination of the Reaction Velocity Constant and Reaction Order of the Oxidation Reaction of Ascorbic Acid

The following (Table III.1) are the results of determining the reaction velocity constant and order of Vitamin C oxidation at 40, 50, 60, 70, and 80 degrees Celsius.

Table III.1 Ascorbic acid percentages at time t for T = 40, 50, 50, 70, and 80 degrees Celsius

Temperature ℃)	Ascorbic acid first	% ascorbic acid left in heating process for (minutes)					
		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

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

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

Temperature ℃)	Ascorbat acid first concentratio	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

From Table III.2 we can see that the data for the initial concentrations of both 0.0412M and 0.0284M ascorbic acid tend to be constant; therefore half-time is independent of initial concentration and initial value. Based on Table III.2, the half-time is between 650 - 1500 minutes; much longer than the data gathered 300 minutes. 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 velocity 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 minutes. The alternative would be to use the half-time method to determine the oxidation reaction of ascorbic acid's reaction order, the results of which are shown in Table III.3, based upon data from Table III.2 and by using Equation (II.1).

Table III.3 Reaction order calculation based on the half-time method at 40 degrees Celsius

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

Data from Table III.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-dychlorophenol indophenol, suggests a first order reaction for temperatures between 4 and 5 degrees Celsius.[13] 2) Vitamin C degradation determined using the potentiometric method at 37.8 amd 46.1 degrees Celsius also suggests a forst order reaction.14] 3) Vitamin C degradation kinetics in storage at temperatures between 25 and 45 degrees Celsius in 5 degree Celsius intervals, respectively, with Vitamin C concentration determined through titration with 2,6-dychlorophenol, suggests a first order reaction.[15]

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

$$k\,\mathrm{t} = \ln \frac{a}{(a - x)} \qquad \text{(III.2)}$$

where a is the (percent) initial concentration of ascorbic acid and (a-*x*) the (percent) ascorbic acid remaining after each time interval. Calculations are shown in Table III.4.

Table III.4 Velocity Constant of the Oxidation Reaction of Ascorbic Acid at Various Temperatures and Time Intervals

No.	t (minutes)	The value of reaction rate constant, *k* (minutes^{-1}) at temperature				
		40^0C	50^0C	60^0C	70^0C	80^0C
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**

Based on these calculations, the velocity constants at 40, 50, 60, 70, and 80 degrees Celsius are 0.00045, 0.00059, 0.00084, 0.00109, and 0.00102 respectively.

III.2 Activation Energy and Pre-exponential Factor Determination

The reaction rate constant data from Table III.4 shows that the rate constant (k) rises with temperature. This is consistent with the Arrhenius Theory. Increased 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 from Table III.4 and using Equation (II.4). Plotting ln *k* against $\frac{1}{T}$ gives Figure III.1.

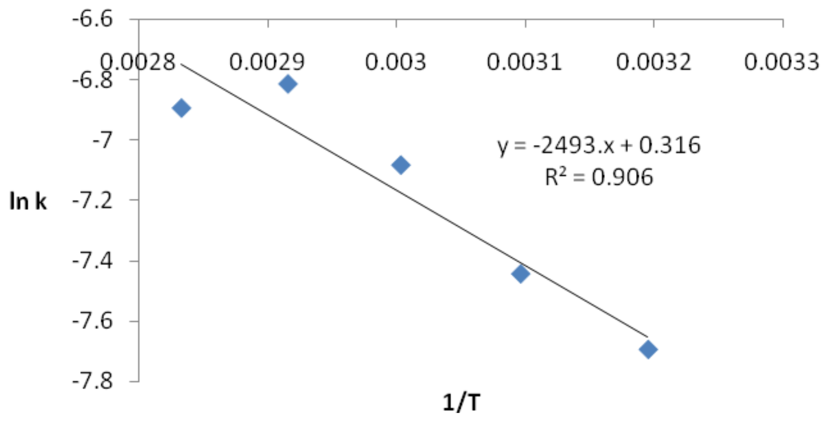

Fig III.1 The relation between ln k and 1/T in the ocidation reaction of ascorbic acid.

From Fig III.1 we can get the regression equation *y* = 0.316 - 2493 x with R^2 = 0.906. based on the regression equation we can get pre-exponential factor of 1.372 minutes $^{-1}$ and activation energy of 20.726 kJ mol^{-1}.

$$\ln A = 0.316 \qquad -\frac{E_a}{R} = -2493$$

$$A = 1.372 \qquad E_a = 2493\,K \; x \; 8.314\; J.K^{-1}.mol^{-1}$$

$$= 20726.8 \;\; J..mol^{-1}$$

$$= 20.73 \;\; kJ..mol^{-1}$$

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

$$k = 13.32 \; e^{\frac{20.73}{RT}} \qquad \text{(III.3)}$$

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

III.3 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 III.5.

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

Basic Competence	Learning Activities	Indicators
3.1 Describing and understanding reaction rate through an experiment investigating the factors that influence reaction rate.	▪ Calculating and making a solution of a specific concentration in groups, in the laboratorium. ▪ Designing and conducting and experiment to investigate the factors that influence reaction rate, in the laboratorium ▪ Concluding the factors that determine reaction rate.	▪ 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.

Learning material dan some reaction kinetics core modules have been designed based on Table III.5. Specifically, the lab module has been designed to include the creation of an ascorbic acid solution at varying concentrations, analyzing the effects of concentration and temperature on the reaction velocity 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°C, 50°C, 60°C, 70°C and 80°C with values of reaction rate constant respectively 4.55 x 10^{-4} $minutes^{-1}$, 5.85x 10^{-4} $minutes^{-1}$, 8.4 x 10^{-4} $minutes^{-1}$, 1.1 x 10^{-3} $minutes^{-1}$, 1.015 x 10^{-3} $minutes^{-1}$ with activation energy of 20.73 kJ mol^{-1}, pre-exponential factor 1.372 $minutes^{-1}$.

Studying 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.

SUGGESTION

For the next research, 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 to be used in high school.

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