

Degradation of Ascorbic acid in Limited Dissolved Oxygen Environment

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=국문 초록=

—제한된 산소 존재중의 Ascorbin 산의 분해에 대하여—

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이 속 회

Vitamin C의 변화는 식품의 가치를 판단하는데 중요한 인자가 된다. 이의 변화는 산소의 존재하에서 일차반응 속도로 분해된다고 알려져 있다. 그러나 제한된 양의 산소속에서는 이차반응 내지 일차반응으로 설명되기도 한다. 이에 제한된 산소속에서 철, 구리 이온의 존재하에서 관찰한 반응은 산소와는 크게 관계없이 일차 반응속도로 분해되었고 이때 빛의 조사는 촉진적인 인자였었다.

Introduction

Nutritional degradation including changes in color or development of off-flavor may occur in food during storage.

The quality deterioration by the reaction are dependent upon many factors. Stull and Wishner reviewed the earlier studies on the influence of fluorescent light on ascorbic acid degradation and development of off-flavor in milk¹⁾.

Dimick studied on off-flavor and degradation of ascorbic acid in milk due to light and dissolved oxygen²⁾.

The deterioration of ascorbic acid in liquid was proportional to the amount of available oxygen. 8.27% loss of ascorbic acid in deaerated milk at 4C for 7 days compared with 57.1% loss of aerated milk was reported by Guthrie³⁾.

The kinetics of auto-oxidation of ascorbic acid in sugar solution in presence of dissolved oxygen was reported by Joslyn and Miller⁴⁾.

The kinetic pattern of oxidation was revealed as

first-order reaction with respect to the ascorbic acid concentration. They also found that the initial rate of oxidation was reduced under the limited oxygen supply.

Tressler and Pederson reported no deterioration of pasteurized grape juice packed in high vacuum or negligible oxygen⁵⁾ Timberlake showed that oxidation of ascorbic acid in the presence of copper and iron was significant and also discussed the effects of some metal chelating agent on ascorbic acid oxidation⁶⁾. Taqui Khan and Martel reported the ascorbic acid oxidation under the various influence of oxygen content in the presence of copper and iron on pH and proposed the model of oxidation of ascorbic acid degradation as first-order or reaction as long as the oxygen was 100-50%⁷⁾. Under the limited content of oxygen, the mechanism of the oxidation of ascorbic acid may become complicated, Hedelman and Kirk also investigated the ascorbic acid oxidation under the limited presence of dissolved oxygen does not follow first-order mechanism and oxygen uptake was analyzed as an overall second order reaction.⁸⁾

The ascorbic acid oxidation under the limited oxygen content and the presence of iron (III) and copper (II) with light, revealed the first-order of reaction by the oxidation including catalytic degradation.

Theoretical considerations.

The period of time required for ascorbic acid to decompose to one-half the original concentration as calculated in the half-life, $t_{1/2}$, for the first order reaction:

$$\ln \frac{C_0}{C} = \ln \frac{C_0}{\frac{1}{2} \cdot C} = \ln 2 = kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

Experimental

Materials The L-ascorbic acid used in this study was Wako Pure Chemical's, and was dissolved in meta-phosphoric acid-acetic acid solution, and diluted to the 0.10% of ascorbic acid. The pH revealed in 2.20 that was stable from auto-oxidation. All experiment was carried out at pH 2.20.

Procedures General day light fluorescent lamps which have 1100 lux in 25cm high were used in this study, and the spectral distribution of these fluorescent lamps were not considered. A reflector-holder with two or four fluorescent lamps were hung from the ceiling. A constant-temperature water-bath was used to control a temperature around the exposure cells.

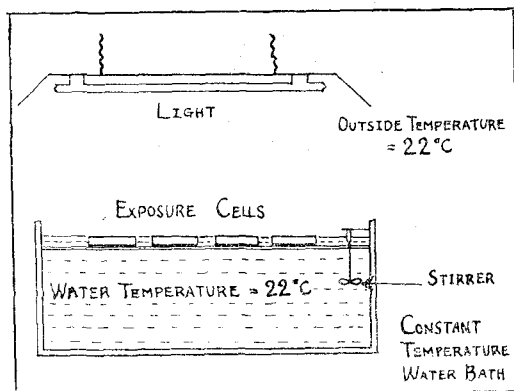


Fig. 1. Experimental Cells Exposed to Light

The exposure cells were petri dishes of 9cm diameter. The cells were arranged on a platform in the constant water bath with their sides submerged in water. After completion of the desired exposure time, the sample was removed from the cell using the volumetric pipet and hypodermic syringe. The sample was then either assayed for ascorbic acid or analyzed for dissolved oxygen concentration.

The following storage experiments were conducted; The two trials with the initial dissolved oxygen concentration of 2.6×10^{-4} , and 1.6×10^{-4} M respectively using the baby air pump. The 50.0ml of sample was saturated with atmospheric air to obtain a dissolved oxygen concentration of 2.6×10^{-4} and 1.6×10^{-4} M (at 22 C water Bath), and was covered with 30ml of liquid paraffin to protect with atmospheric oxygen.

All storage experiment was conducted at 22 C and under the four fluorescent lamps and dark in brown color bottle without light. The vitamin assay and dissolved oxygen measurement were conducted on duplicate samples at 10, 20, 30, 40, 50 and 60 hours storage duration. The ascorbic acid assay procedure is conducted by indophenol method in AOAC.⁹⁾ The dissolved oxygen measurements were conducted using the precision Galvanic Cell Oxygen Analyzer.

Results and Discussion

Spontaneous Oxidation The rate profile of spontaneous oxidation of ascorbic acid on the various pH at 25 C in the large excess of oxygen were in Figure 2. So the working pH of 2.20 was very stable against auto-oxidation.

Oxygen, Light and Copper(II), Iron(III) catalyzed oxidation To determine the order of reaction, the measured ascorbic acid concentration in the samples with initial dissolved oxygen content of 2.6×10^{-4} M, and 8.0×10^{-5} , 1.6×10^{-5} , and 4.0×10^{-6} M of iron(III), and 9.0×10^{-5} , 1.8×10^{-5} , and 4.5×10^{-6} M of copper(II) under the four fluorescent lamps are plotted in figure 3 and the plots

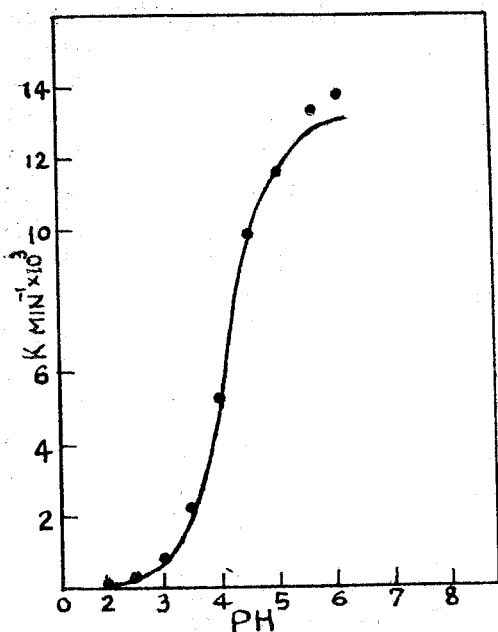


Fig. 2. Rate Profile for the Spontaneous Oxidation of Ascorbic Acid at 25C

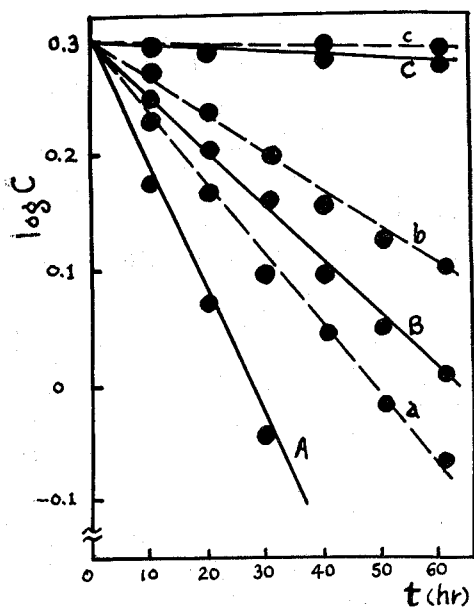


Fig. 3. Catalytic Effect for the Oxidation of Ascorbic Acid in the Presence of Copper(II) and Iron(III) under the Four Fluoroscopic Lamps in the Initial Dissolved Oxygen Content $2.6 \times 10^{-4}M$, A; $8.0 \times 10^{-5}M$, B; $1.6 \times 10^{-5}M$, C; $4.0 \times 10^{-6}M$ of Copper(II), and a; $9.0 \times 10^{-5}M$, b; $1.8 \times 10^{-5}M$, c; $4.5 \times 10^{-6}M$ of Iron(III).

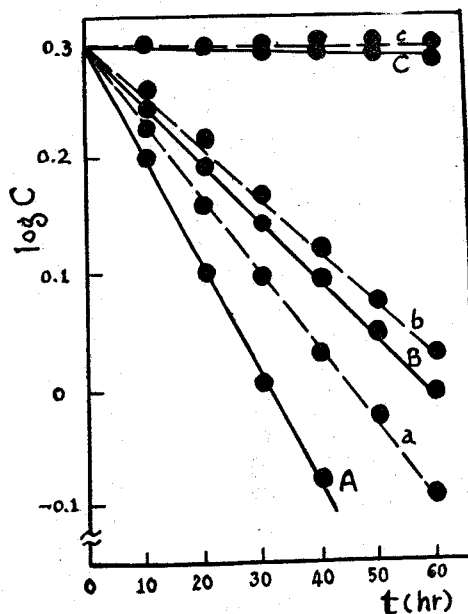


Fig. 4. Catalytic Effect for the Oxidation of Ascorbic Acid in the Presence of Copper(II) and Iron(III) under the Four Fluoroscopic Lamps in the Initial Dissolved Oxygen Content $1.6 \times 10^{-4}M$, A; $8.0 \times 10^{-5}M$, B; $1.6 \times 10^{-5}M$, C; $4.0 \times 10^{-6}M$ of Copper(II) and a; $9.0 \times 10^{-5}M$, b; $1.8 \times 10^{-5}M$, c; $4.5 \times 10^{-6}M$ of Iron(III).

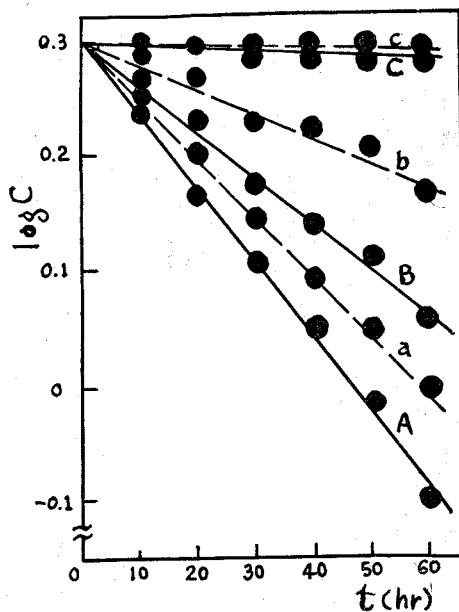


Fig. 5. Catalytic Effect of the Oxidation of Ascorbic Acid in the Presence of Copper(II) and Iron(III) in, Dark the Initial Dissolved Oxygen Content $2.6 \times 10^{-4}M$, A; $8.0 \times 10^{-5}M$, B; $1.6 \times 10^{-5}M$, C; $4.0 \times 10^{-6}M$ of Copper(II) and a; $9.0 \times 10^{-5}M$, b; $1.8 \times 10^{-5}M$, c; $4.5 \times 10^{-6}M$ of Iron(III).

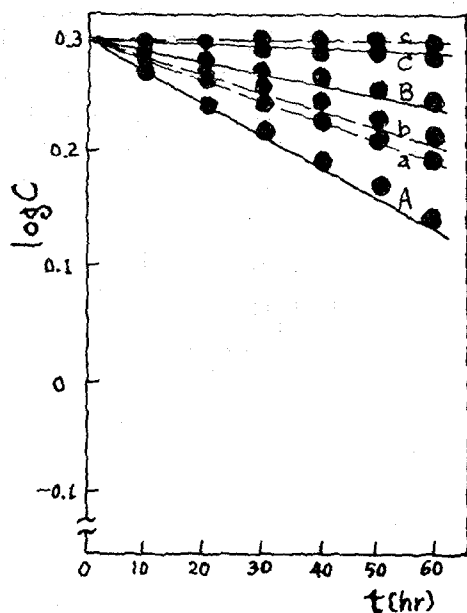


Fig. 6. Catalytic Effect for the Oxidation of Ascorbic Acid in the Presence of Copper(II) and Iron in Dark in the Initial Dissolved Oxygen Content $1.6 \times 10^{-4}M$. A; $8.0 \times 10^{-5}M$, B; $1.6 \times 10^{-5}M$, C; $4.0 \times 10^{-6}M$ of Copper(II) and a; $9.0 \times 10^{-5}M$, b; $1.8 \times 10^{-5}M$, c; $4.5 \times 10^{-6}M$ of Iron(III).

of the initial dissolved oxygen content of $1.6 \times 10^{-4}M$ and 9.0×10^{-5} , 1.8×10^{-5} , and $4.5 \times 10^{-6}M$ of copper(II) were in figure 4.

It is apparent when dissolved oxygen was present in a little higher of $1.0 \times 10^{-4}M$, the reaction can be considered to be little faster and catalytic oxidation of reaction can be considered to follow first-order of mechanism in 60 hours, whereas the control and metal masking agent of EDTA added were quite stable in 60 hours.

However, under the limited presence of oxygen and light, the data fit a straight-line on log coordinates and hence follow a first-order mechanism when the catalysts such as copper(II) and iron(III) were present.

Therefore, the reaction was assumed to follow an overall an overall first-order kinetics. The calculated first-order rate constant for two initial dissolved oxygen concentrations and the light are

Table 1. First-Order Rate Constants of Ascorbic Acid Degradation Exposed to Four Fluorescent Lamps Light Intensity

Catalyst	*I.D.O.: 2.6×10^{-4}		I.D.O.: 1.6×10^{-4}		
	Light	Dark	Light	Dark	
Copper (II)	A	2.47×10^2	1.54×10^2	2.17×10^2	6.54×10^3
	B	1.10×10^2	9.49×10^1	1.14×10^2	2.51×10^3
	C	1.54×10^2	8.15×10^1	1.18×10^2	3.85×10^4
Iron (III)	a	1.43×10^2	1.20×10^2	1.98×10^2	4.25×10^3
	b	7.37×10^1	4.88×10^1	1.08×10^2	3.67×10^3
	c	7.62×10^1	5.33×10^1	6.30×10^1	3.30×10^4

*I.D.O- Initial Dissolved Oxygen

A; $8.0 \times 10^{-5}M$ a; $9.0 \times 10^{-5}M$
 B; $1.6 \times 10^{-5}M$ b; $1.8 \times 10^{-5}M$
 C; $4.0 \times 10^{-6}M$ c; $4.5 \times 10^{-6}M$

presented in Table 1.

The rate constant based on the average duplicate trials with the measurement of half-life determination during storage. The decrease of dissolved oxygen concentration from $2.6 \times 10^{-4}M$ to $1.6 \times 10^{-4}M$ in the samples exposed to light resulted in decreased rate constants. The little variation of rate constant on the variation of oxygen content, the dehydroascorbic acid which is the product of ascorbic acid by dissolved oxygen content take a great part of catalytic oxidation of ascorbic acid. It may be attributed to side reactions of same type as suggested by Weissberger et al.¹⁰⁾

Catalytic oxidative ability in copper(II) was much higher than that of iron(III), and the catalytic oxidative reaction rate constant was increased in proportion to the content of metal ion during the higher content of dissolved oxygen was present in samples.

However, there was no significant difference in rate constant for samples in reduces of $1.6 \times 10^{-4}M$ of reduced initial dissolved oxygen content in Iron(III) compared with copper(II). So, copper(II) was assumed to be not influenced by dissolved oxygen content on catalytic degradation on ascorbic acid so greatly than iron(III).

Conclusions

1. The Ascorbic acid degradation under the limited oxygen content can be described by an overall first-order reaction when catalyst such as copper (I) and iron(III) was present.

2. An increase in initial dissolved oxygen concentration from 1.6×10^{-4} to 2.6×10^{-4} M and exposed to light resulted in increased first-order rate constants. The rate constants under dark as control for different initial dissolved oxygen concentration were also increased a little, however, copper ion was more effective than iron in decreased environment of oxygen.

3. The first-order rate constant increases in proportion to the increase of metal ion concentration, however, metal ion concentration, however, metal ion concentrations of 4.0×10^{-6} M of copper(II), and 4.5×10^{-6} M of iron(III) are almost meaningless within 60 hours.

Summary

Deterioration of ascorbic acid content is the important factor in the food quality. The degradation of ascorbic acid undergoes as a first-order of reaction in the presence of excess oxygen content. However, under the limited oxygen content, ascorbic acid decomposes as a pseudo-first order of

reaction.

The ascorbic acid, in this study, under the limited dissolved oxygen content in the presence of iron(III) and copper(II) decomposed as first-order reaction with a little influence in rate constant and the light was an accelerating factor on the ascorbic acid degradation.

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