

Kinetic and Energetic Correlations in the Reaction of Vitamin-C Tablets

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Authors' contributions

This work was carried out in collaboration between both authors. Author SMA designed the study, performed the statistical analysis. Author MMS wrote the protocol and wrote the first draft of the manuscript. He sent the article to the journal and reviewed it to reach the final proof. Both authors read and approved the final manuscript.

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ABSTRACT

The oxidation time based on the fitting of experimental data was taken out. Drawing of the Absorbance ($\lambda_{\max}=265$ nm) vs. oxidation time (sec) of Vitacid C by K_2CrO_4 were studied. Energy consumed during oxidative degradation of vitamin-C(Vit-C) Tablets in aqueous potassium chromate (K_2CrO_4) medium was studied spectrophotometrically at 25°C. The reduction of the absorbance at 265 nm with increasing time was scanned. A good linearity (R-square ≥ 0.99). The slope (EC/ppm) vs reductant (Vit-C/ppm) at constant oxidant is about 1.218, while, the slope of EC vs. oxidant (K_2CrO_4 /ppm) is about 3.653. Calculations suggest that the EC during reduction of Cr (VI) to Cr (III) is about three times of magnitude faster than the oxidation of the Vit - C sample.

Keywords: Ascorbic acid(H_2A); Hexacyanoferrate(III); kinetics; oxidation; mechanism.

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1. INTRODUCTION

Ascorbic acid is a white crystalline and odourless substance. Due to its polar characteristics, it is easily soluble in water and its solubility in nonaqueous media, such as ethanol and acetonitrile, is quite limited. The crystalline and pure ascorbic acid is stable when exposed to air, light, and ambient temperature for a long period [1]. Vitamin C is the generic kind of all compounds exhibiting qualitatively the biological activity of ascorbic acid. It suffices as a water-soluble antioxidant by reacting with free radicals and reducing reactive oxygen species to protect against the oxidation of lipids, proteins, and DNA [2]. The non-isothermal aerobic degradation of ascorbic acid (AA), and the organization and subsequent degradation of the dehydroascorbic acid (DHAA) are distinguished by two simultaneous rate equations. Also accepted is that the temperature-dependence of these three reactions' rate-constants follows the exponential model, a simpler substitute for the traditional Arrhenius equation [3]. Vitamin C and its degradation products participate in chemical modifications of proteins *in vivo* through non-enzymatic glycation (Maillard reaction) and formation of different products called advanced glycation end products. The identification of 3-deoxythreosone as the major degradation product bound to human lens proteins provides *in vivo* evidence for the non-oxidative pathway of dehydroascorbate degradation into erythrulose as a major pathway for vitamin C degradation *in vivo* [4]. Matei et al. [5] determinate the rate constant, the half-time and the activation energy for vitamin C. It can take note that the rate constants depend strongly on temperature, typically increasing rapidly with increasing T. It can take note that the values of the activation energy, analytical and graphical determined are in good agreement. The dynamics of vitamin C have been examined extensively in model systems with exceptional care to intermediate moisture foods and during storage studies. Hence, it is necessary to study the subject of different processing temperatures on the retention of vitamin C in the product and kinetic modelling to anticipate the losses during processing by different heating methods [6]. Cyclic Voltammetry was used to examine the kinetics of degradation of ascorbic acid (AA) at different temperatures. It has been shown that the reduction of the concentration of AA in all temperatures follows the dynamics of the first order reaction. The kinetics of degradation of vitamin C was also studied using titrimetric and

spectrophotometric methods [7]. The decision of the dynamics of the oxidation of ascorbic acid applies the integral and half-change time methods, while the compactness of the remained ascorbic acid in sixty minute intervals is determined by iodometric titration method. Pre-exponential factor or the frequency of collisions is a factor which is a quantity of the collision rate. The activation energy and the pre-exponential factor for the oxidation of ascorbic acid were calculated [8]. In parliamentary law to compare the data published, the rate constants of degradation have been estimated assuming the first-order kinetics of degradation [9]. It has been established that temperature, the form of vitamin and the matrix are the factors affecting most the stability of vitamin C in foods and drinks. Lower storage temperature brings about a higher retention of vitamin C. The matrix also affects the rate constants of degradation. For liquid matrices and for comparable temperatures, the rate constants are much higher for the degradation in milk than in fruit juices and drinks. Equally, for the solid matrices, the rate constants of vitamin C degradation in bread are from 2–3 orders of magnitude higher than those for the bran flakes, grains, dried apple chips and potato chips. Lanny et al. [10] study the kinetics of degradation of vitamin C in fresh strawberry juices upon storage and to investigate the result of storage temperatures and sugar added to the ascorbic acid loss in strawberry juices. The results showed that the degradation reaction of vitamin C followed zero-order kinetic models in all types of juices. The activation energy for vitamin C degradation in fresh strawberry juices with sugar and without the sugar addition was estimated to be 1.90 kcal/ mol and 1.65 kcal/ mol, respectively. The degradation kinetics of vitamin C and colour in terms of a reaction rate constant, destruction kinetics, enthalpy and entropy for different methods of heating discussed [11]. The destruction of vitamin C was influenced by the method of heating and the temperature of processing. The degradation was highest during microwave heating due to uncontrolled temperature generated during processing. The visual colour has generally used an index of the carotenoid content. The activation energies for both vitamin and colour were within the range of literature reported values of 7.54–125.6 KJ/Mol. The rate of vitamin C degradation in the Lettuce and Cabbage samples under the same processing method was investigated [12]. The rate of degradation is dependent on the concentration of the vitamin C present in both vegetables. This impresses the fact that the

blanching of Cabbage at 70°C of water is more preferable in terms of vitamin C retention than Lettuce, hence, is recommended for food supplement Industries to deploy this research findings for further processing into semi and finished products after dehydration because degradation of vitamin C during processing might be a critical factor for the shelf life of some products such as nutrient concentrates, since vitamin C content of fruits undergoes destruction during processing and storage .In this study, Energy consumed during oxidative degradation of vitamin-C (Vit-C) Tablets in aqueous potassium chromate (K₂CrO₄) medium was studied spectrophotometrically.

2. MATERIALS AND METHODS

2.1 Solutions and Chemicals

Vitacid C (Vit-C) Tablets was purchased for Chemical Industries Development (CID), Giza-Egypt-G. C. R. 19717. Stock solutions of Vit-C and potassium chromate (K₂CrO₄) Aldrich, Milwaukee, WI) were set up by dissolving a single tablet or appropriate amount of the respective samples in double distilled water. L-Ascorbic acid (L-Asc) was purchased from Merck, Germany. Solutions of H₃PO₄, NaH₂PO₄, Na₂HPO₄, and Na₃PO₄ were used for the preparation of buffer media. All other reagents used were of analytical grade.

2.2 Instrumentation

Thermo Electron-Vision pro Software V 4.10 UV/Vis spectrophotometer (190–1100 nm) with 1.0 cm quartz cell (scan speed, H₃PO₄, 8.0nms⁻¹) was used for spectrophotometric measurements.

2.3 Procedure

Ten milliliters of 1.0 mmol L⁻¹ solution of K₂CrO₄ (oxidant) in strong acid was placed in into a calibrated flask. The background spectrogram of this solution was recorded. Then, different amounts of the analyte (Vitacid C Tablet, Vit-C) were added into individual flasks by means of a

micropipette (Waco, UK). All presented absorption spectra are corrected for the blank reagent, which was made in a similar way as the samples, all the same, not containing the analyte. All measurements were carried out at room temperature (21±1°C).

2.4 Method of Calculations

Molecular Mechanics (MM+) calculation, including MM2 and MMP2 force field [13-15] were carried out assuming the investigated molecule in the gas phase. The values of potential and geometric energies as well as the dipole moment were obtained considering dPE ¼ 0.42 J and the normal method. The search for a minimum energy of the molecule geometry resulted in a 3D structure. MM+ calculations iteratively change the location of particles towards the structure characterized by lower energy until the molecular internal energy has been downplayed. The potential energy of a molecular system is a function of the atomic coordinates [16-18]:

$$E_{(x)} = E_{str} + E_{ang} + E_{stb} + E_{oop} + E_{tor} + E_{vdw} + E_{ele} + E_{sol} + E_{res} \quad (1)$$

$$E_{str} = W_{str} \sum_{i-j-k} (K_{ij}) (r_{ij} - L_{ij})^2 + K_{ij} (r_{ij} - L_{ij})^3 + K_{ij} (r_{ij} - L_{ij})^4 \quad (2)$$

$$E_{ang} = W_{ang} \sum_{i-j-k} (K_{ijn}) d_{ijk}^2 + K_{ijk}^2 d_{ijk}^3 + K_{ijk}^3 d_{ijk}^4 \quad (3)$$

$$E_{stb} = W_{stb} \sum_{i-j-k} \{ (K_{ijk}) (r_{ij} - L_{ij}) + K_{ijk} (r_{jk} - L_{jk}) \} d_{ijk} \quad (4)$$

$$E_{oop} = W_{oop} \sum_{ijkl} X_{ijkl}^2 \quad (5)$$

$$E_{tor} = W_{tor} \sum_{i-j-k-l} \sum_{n=0}^6 (K_{ijn}) \cos (nT_{ijkl} - P_{nkl}) \quad (6)$$

$$E_{vdw} = W_{vdw} \sum_{i<j} (e_{ij}) \left[\frac{(1+a)R_{ij}}{r_{ij} + aR_{ij}} \right]^{n_{ij}} \left[\frac{(1+b)R_{ij}^{m_{ij}}}{r_{ij}^{m_{ij}} + bR_{ij}^{m_{ij}}} - \frac{m_{ij} + n_{ij}}{m_{ij}} \right] S(r_{ij}) T_{ij}^{vdw} \quad (7)$$

$$E_{ele} = \begin{cases} \frac{W_{ele} e^2}{4\pi\epsilon_0 d} \sum_{i<j} q_i q_j \left[\frac{1}{r_{ij} + b_{ij}} \right] S(r_{ij}) T_{ij}^{ele} & \text{Coulomb} \\ \frac{W_{ele} e^2}{4\pi\epsilon_0 d} \sum_{i<j} q_i q_j \left[\frac{1}{(r_{ij} + b_{ij})^2} \right] S(r_{ij}) T_{ij}^{ele} & \text{Distance Dependent Dielectric} \\ \frac{W_{ele} e^2}{4\pi\epsilon_0 d} \sum_{i<j} q_i q_j \left[\frac{1}{r_{ij} + b_{ij}} - \frac{\infty_{ij}^2}{R_c^2} - \frac{(1-\alpha)}{R_c} \right] S(r_{ij}) T_{ij}^{ele} & \text{Reaction Field, } x = \frac{d-d_x}{d-2d_x} \end{cases} \quad (8)$$

$$E_{\text{sol}} = -w_{\text{sol}}W(d^{-1} - d_x^{-1}) \frac{e^2}{4\pi\epsilon_0} \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \frac{q_i q_j \sqrt{G_i G_j}}{\sqrt{y_{ij} + \exp(-y_{ij})/4}} S(r_{ij}) T_{ij} \cdot y_{ij} = r_{ij}^2 G_i G_j \quad (9)$$

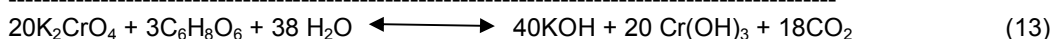
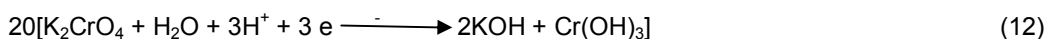
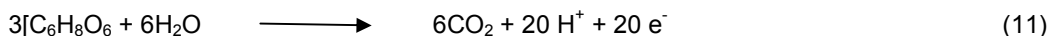
$$d_q = \frac{1}{2} + \frac{X_i - X_j}{X_j^+} \quad (10)$$

E_{str} is the bond stretch, E_{ang} is the bond angle bend; E_{stb} is the stretch-bend, E_{oop} is the out-of-plane, E_{tor} is the torsion, E_{vdw} is the van der Waals force, E_{ele} is electrostatic, E_{sol} is the implicit solution, E_{res} is restraint energy, and X_j^+ is the electronegativity of the positive ion of atom.

3. RESULTS AND DISCUSSION

3.1 Oxidative Degradation Mechanism of Vit-C by K_2CrO_4

The absorption spectra of Vit-C (Vitacid concentration: $16.8 \times 10^{-5} \text{ molL}^{-1}$) after different addition of K_2CrO_4 ($2 \times 10^{-5} \text{ molL}^{-1}$) were studied (Time effect, $t = 1 \text{ min}$) as shown in Fig. 1a. The decreases of the absorbance rapidly with increasing the concentration of K_2CrO_4 could be attributed to the oxidative degradation of Vit-C according to the following mechanism:



The maximum was shifted to the higher wavelength ($\lambda_{\text{max}} \approx 285 \text{ nm}$) via the first derivative (D_1). This shift indicates that the higher derivative is more sensitive than D_0 derivative (normal spectra) as shown in Fig. 1b.

3.2 Oxidation time of Vit-C in Aqueous Media

The oxidation time based on the fitting of experimental data obtained. For example, when oxidative degradation of Vit-C (0.5 mmol L^{-1}) by $KMnO_4$ ($0.05, 0.1, 0.15, 0.2, 0.25,$ and 0.3 mmol L^{-1}) was carried out. Computer drawing of the Absorbance (A: a-f) ($\lambda_{\text{max}} = 265 \text{ nm}$) vs. oxidation time (sec) of Vitacid C by K_2CrO_4 as shown in Fig. 2. The reaction rate constant ($k^{1/4}$) $2.207 \times 10^{-4} \text{ s}^{-1}$ was computed and the values of statistical parameters $r^{1/4}$ 0.989 and $RSD^{1/4}$, 2.23×10^{-4} were obtained. While, Computer drawing of the integrated A ($\lambda_{\text{max}} = 265 \text{ nm}$) vs. oxidation time (sec) of Vitacid C by K_2CrO_4 is shown in Fig. 3. The limit of detection can be as low as 18 ppm (mg L^{-1}) of Vit-C, suggesting the

possible application of this procedure for the determination of Vit-C in real samples.

3.3 Energy Consumed (EC) of Vit-C in Aqueous Medium

The fundamental property of an electrically activated chromogenic material is that it exhibits a large change in optical properties upon a change in either electrical field, injected or ejected charge. The increases of EC with increasing of Vit-c at constant oxidant (K_2CrO_4) or at constant Vit-C with increasing K_2CrO_4 were recorded as seen in Table 1.

A good linearity ($R\text{-square} \geq 0.99$) as shown in Fig. 4. The slope (EC/ppm) vs reductant (Vit-C/ppm) at constant oxidant is about 1.218, while, the slope of EC vs. oxidant (K_2CrO_4 /ppm) is about 3.653 (Table 2). These calculations indicate that the EC during reduction of Cr(VI) to Cr(III) is about three times of magnitude faster than the oxidation of Vit-C sample.

Table 1. Variation of energy consumed (EC) during oxidation of Vit-C or K_2CrO_4

Vit-C (ppm)	17.62	26.41	35.20	44.10	52.80	61.10	70.48
E.C (kcal kg^{-1} h)	4.016	12.92	23.86	34.92	45.74	56.06	67.72
K_2CrO_4 (ppm)	9.71	19.42	29.13	38.34	48.56	58.26	67.97
E.C (kcal Kg^{-1} h)	96.21	140.07	173.37	206.06	241.69	282.13	313.02

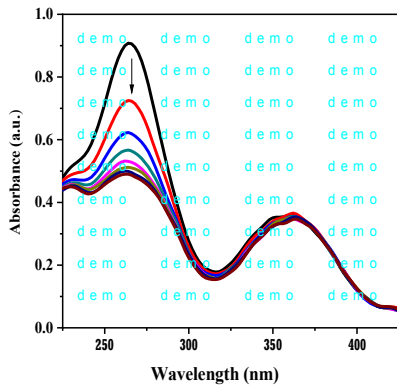


Fig. 1a. Absorption spectra of Vit-C in the presence of oxidant (K_2CrO_4)

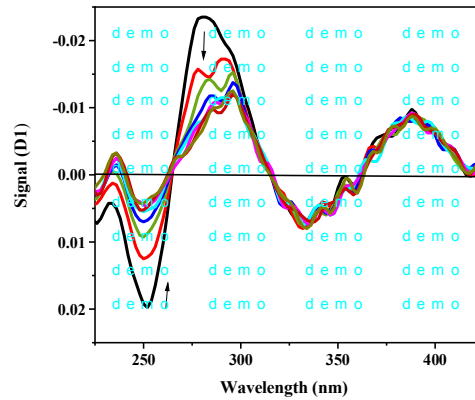


Fig. 1b. First derivative of 1a

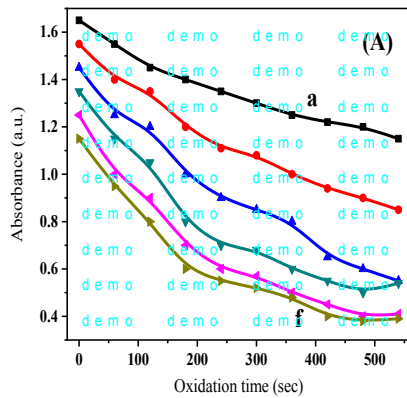


Fig. 2. Computer drawing of the absorbance (A) ($\lambda_{max}=265\text{ nm}$) vs. oxidation time (sec) of Vitacid C (0.5 mmol/L) by K_2CrO_4

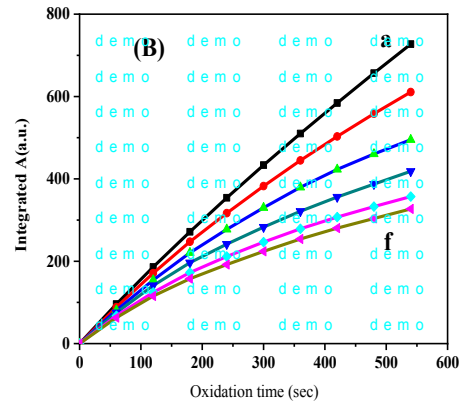


Fig. 3. Computer drawing of the integrated A ($\lambda_{max}=265\text{ nm}$) vs. oxidation time (sec) of Vitacid C (0.5 mmol/L) by K_2CrO_4

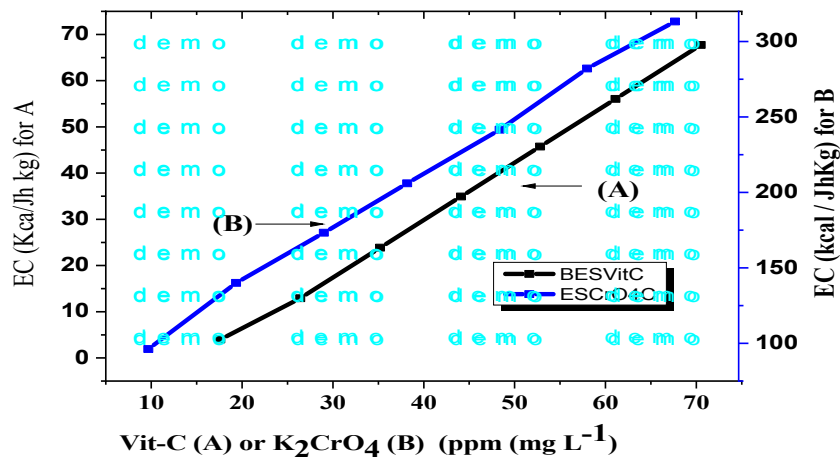


Fig. 4. Variation of energy consumed (EC) vs. Vit-C (ppm) for A, and K_2CrO_4 (ppm) for B

Table 2. Calibration plot data of the variation EC during oxidation of Vit-C or K₂CrO₄-Matrix

K ₂ CrO ₄ -Matrix	Slope (kcal kg ⁻¹ h ppm ⁻¹)	Correlation coefficient Adj-R-Square	Standard error (RSD)
EC vs. Vit-C	1.21872	0.9991	0.01424
EC vs. K ₂ CrO ₄	3.69107	0.9983	0.06173

4. CONCLUSIONS

Computer drawing of the Absorbance ($\lambda_{\max}=265$ nm) vs. oxidation time (sec) of Vitacid C by K₂CrO₄ was computed. Energy consumed during oxidative degradation of vitamin-C (Vit-C) in aqueous potassium chromate (K₂CrO₄) medium has been studied spectrophotometrically and computationally. The decrease of the absorbance at ~ 265 nm with increasing time was scanned. A good linearity (R-square \geq 0.99). The slope (EC/ppm) vs reductant (Vit-C/ppm) at constant oxidant is about 1.218, while, the slope of EC vs. oxidant (K₂CrO₄/ppm) is about 3.653. Calculations indicate that the EC during reduction of Cr (VI) to Cr (VI) is about three times of magnitude faster than the oxidation of the Vit - C sample.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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