Journal of Pharmaceutical and Biomedical Analysis 59 (2012) 190–193

Contents lists available at SciVerse ScienceDirect

Journal of Pharmaceutical and Biomedical Analysis

journal homepage: www.elsevier.com/locate/jpba

Short communication

Thermal stability of vitamin C: Thermogravimetric analysis and use of total ion monitoring chromatograms

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ARTICLE INFO

Article history:
Received 10 May 2011
Received in revised form 11 October 2011
Accepted 13 October 2011
Available online 20 October 2011

Keywords:
L-ascorbic acid
Decomposition kinetic
Shelf life
Arrhenius parameters
TGA
EGA–Li$^+$IAMS

ABSTRACT

The thermal decomposition kinetics and shelf life of vitamin C in nitrogen or air were studied by using thermogravimetric analysis (TGA) and evolved-gas analysis–lithium-ion attachment mass spectrometry (EGA–Li$^+$IAMS). Arrhenius parameters obtained via TGA were reported for thermal decomposition. For vitamin C in a nitrogen atmosphere, the activation energy (E_a) was 25.1 kcal/mol and the pre-exponential factor (A) was 2.5×10^{11} min^{-1}. The kinetic parameters estimated via TGA agreed with values estimated from a pyrogram when the weight loss observed by TGA was shown to be due to gas evolution as a result of decomposition of the compound. Thermal stability was expressed by calculating the time for 10% of the vitamin C to decompose at 25 °C ($t_{90\%,25\,^\circ C}$). The $t_{90\%,25\,^\circ C}$ for vitamin C obtained via TGA or EGA–Li$^+$IAMS was higher in nitrogen (2.0 and 2.0 years, respectively) than in air (1.3 and 1.6 years, respectively). This indicates that the type of atmosphere influences vitamin C stability.

1. Introduction

Vitamin C is important as a pharmaceutical agent, cosmetic ingredient, and dietary supplement. Products containing vitamin C are often subjected to thermal treatment during preparation, processing, and storage [1–5], so it is important to ascertain vitamin C's thermal decomposition kinetics and shelf life. Thermal stability is of particular interest because the results of thermal decomposition kinetic studies may lead to improvements in the stability of the formulations of many pharmaceutical and food products.

Studies on decomposition kinetics of vitamin C in various food products under different storage and processing conditions revealed that decomposition of vitamin C follows first order kinetics and the temperature dependence of the rate of reaction is described by the Arrhenius equation [1–5].

A number of instrumental methods, such as differential scanning calorimetry, differential thermal analysis, and thermogravimetric analysis (TGA), are available for the study of decomposition kinetics. Recently, evolved-gas analysis–mass spectrometry, which is considered to be the second generation of pyrolysis mass spectrometry, has been successfully applied to characterization of the thermal decomposition process [6–9]. In addition, total ion monitoring (TIM) or selected ion monitoring (SIM) chromatograms against temperature can be used as alternatives to pyrograms to provide information for thermal decomposition kinetic studies.

This paper presents the thermal decomposition kinetics (E_a, A) and shelf life ($t_{90\%,25\,^\circ C}$) predictions for vitamin C in nitrogen or air, as obtained via TGA or EGA–Li$^+$IAMS. This paper also compares the TGA method with the EGA–Li$^+$IAMS method with regards to the determination of thermal stability.

2. Methods

2.1. Thermogravimetric analysis and evolved-gas analysis–lithium-ion attachment mass spectrometry (EGA–Li$^+$IAMS)

TGA was conducted with a Shimadzu DT-40 Thermal Analyzer (Shimadzu, Kyoto, Japan) under a nitrogen or air atmosphere at a flow rate of 80 mL/min. Vitamin C samples of 3 mg were heated from 50 °C to 500 °C at a rate of 4 °C/min. EGA–Li$^+$IAMS experiments were conducted with a Li Ion Attachment Mass Spectrometer (Canon ANELVA Corporation, Kanagawa, Japan) and samples of 0.1 mg were heated from 50 °C to 500 °C at a rate of 4 °C/min under a nitrogen or air atmosphere.

3. Results and discussion

3.1. Thermogravimetric analysis

In a nitrogen atmosphere (Fig. 1(a) solid line), vitamin C started to decompose at approximately 191 °C, with the maximum rate

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doi:10.1016/j.jpba.2011.10.011

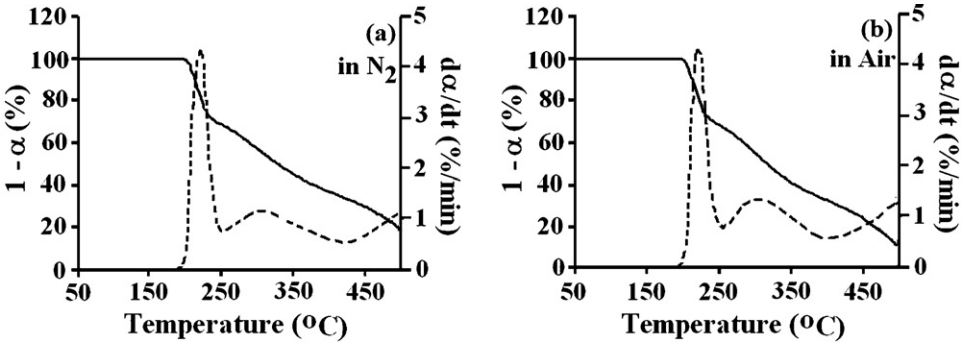

Fig. 1. TG and DTG curves for vitamin C heated in nitrogen (a) and air (b) from 50 °C to 500 °C at a rate of 4 °C/min at atmospheric pressure. DTG curves are represented by a dotted line.

of decomposition occurring at approximately 221 °C. This maximum was followed by two additional decomposition steps in the 251–500 °C temperature range. At 500 °C approximately 11% of the initial sample remained as charred residue.

In an air atmosphere (Fig. 1(b) solid line) degradation also took place in three stages. The decomposition profile was similar to that observed in nitrogen, although the temperature of the initial weight loss (188 °C) was lower than that recorded in nitrogen (191 °C) and at 500 °C approximately 4% of the initial sample remained as charred residue. Since vitamin C is sensitive to the presence of oxygen [10], it is reasonable to expect that, in air, vitamin C starts to decompose at lower temperatures and at a higher rate than in nitrogen.

3.2. Evolved-gas analysis–lithium-ion attachment mass spectrometry

The TIM curves (Fig. 2) closely reproduced the three maxima appearing in the DTG curves (Fig. 1(a and b) dotted line) owing to the evolution of thermal decomposition products. Under EGA–Li$^+$IAMS conditions, vitamin C starts decomposing at lower temperatures than under TG conditions.

In a nitrogen atmosphere (Fig. 2(a)), the initial weight loss started at 182 °C and at 500 °C approximately 5% of the initial sample remained as charred residue while in air (Fig. 2(b)), the first decomposition step of the vitamin C thermal decomposition process started at approximately 180 °C and at 500 °C approximately 2% of the initial sample remained as charred residue.

3.3. Decomposition kinetics analysis

TIM chromatograms obtained from the EGA–Li$^+$IAMS give the relative number of decomposition product molecules, thereby indicating the production rate. The degree of conversion (α) at any temperature (T) is equal to the integrated area under the TIM curve between the temperature at the signal start (T_0) and T. Assuming a first-order reaction [11,12], the ionic signal acquired from real-time total-ion monitoring of chemicals released from a thermally decomposing specimen was used to obtain the functional forms of the following kinetic rate equation:

$$\ln\left[\frac{(d\alpha/dT)\beta}{(1-\alpha)}\right] = \ln A - \frac{E_a}{RT} \quad (1)$$

where α is the degree of yield of the decomposed specimen, T is the temperature, β is the heating rate, A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. Activation energy and pre-exponential factor were determined from plots of $\ln[(d\alpha/dT)\beta/(1-\alpha)]$ versus $1/T$.

In TGA, the DTG plot acquired from real-time weight loss due to the release of chemicals from the thermally decomposing sample was used to obtain the functional forms of the kinetic rate expression.

We evaluated the kinetic data from both the DTG and the TIM curves of the first decomposition step, since these curves represented the most substantial rate of decomposition. We investigated the decomposition kinetics over the 181–231 °C temperature range in nitrogen or in air to obtain rate expressions for vitamin C degradation. The slopes of the plots of temperature versus signal intensity were constant (Fig. 3(a–d)). Activation energies and pre-exponential factors were calculated from the plots (Table 1).

The activation energies for the thermal decomposition of vitamin C obtained from both the TGA and EGA–Li$^+$IAMS experiments were lower in air than in nitrogen. These results were expected, since the initial temperatures for vitamin C decomposition were

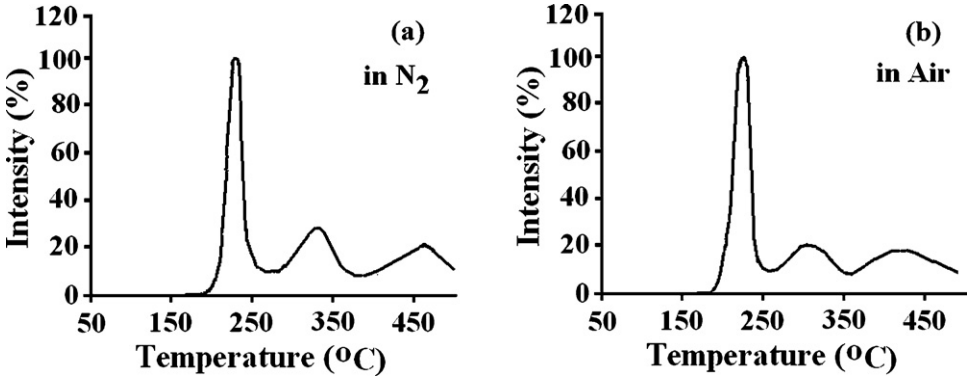

Fig. 2. TIM curves for vitamin C heated in nitrogen (a) and air (b) from 50 °C to 500 °C at a rate of 4 °C/min at *ca.* 40 Pa.