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Kinetic modelling of ascorbic and dehydroascorbic acids concentrations in a model solution at different temperatures and oxygen contents

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ABSTRACT

The degradation kinetics of vitamin C (ascorbic and dehydroascorbic acids, AA and DHA) were determined under controlled conditions of temperature (50–90 °C) and oxygen concentrations in the gas phase (10–30% mol/mol) using a specific reactor. The degradation of vitamin C in malate buffer (20 mM, pH 3.8), mimetic of an apple puree, was assessed by sampling at regular intervals and spectrophotometric quantification of AA and DHA levels at 243 nm. The results showed that AA degradation increased with temperature and oxygen concentration, while DHA exhibited the behaviour of an intermediate species, appearing then disappearing. A kinetic model was successfully developed to simulate the experimental data by two first order consecutive reactions. The first one represented AA degradation as a function of temperature and concentration in dissolved oxygen, and the second reflected DHA degradation as a function of temperature only, both adequately following Arrhenius' law.

1. Introduction

Most fresh fruits and vegetables contain high levels of vitamin C which are of particular importance for human health. Vitamin C has many well-established biological functions that are essential to enzymatic and cellular metabolisms. Its deficiency slows down the activity of several enzyme systems involved in the synthesis of collagen, and causes scurvy (Institute of Medicine, US, Panel on Dietary Antioxidants and Related Compounds, 2000; Patil, Jayaprakasha, Murthy, and Vikram, 2009; Shashirekha, Mallikarjuna, and Rajarathnam, 2015). Vitamin C acts as an antioxidant, having a potentially protective role against cardiovascular diseases and certain cancers (Block, 1991; Frei, Birlouez-Aragon, and Lykkesfeldt, 2012; Patil et al., 2009). It can also be added to fruit-based products to fortify their vitamin levels, as well as an antioxidant to prevent enzymatic browning or oxidation of nutrients or flavours.

For nutritional purposes, vitamin C refers to the sum of L-ascorbic acid (the reduced form, denoted hereinafter as AA), and dehydroascorbic acid (the oxidized form, denoted hereinafter as DHA) (Barrett and Lloyd, 2012). AA is a quite unstable compound and its degradation is closely dependent on environmental conditions such as pH (Golubitskii, Budko, Basova, Kostarnoi, and Ivanov, 2007; Van den Broeck, Ludikhuyze, Weemaes, Van Loey, and Hendrickxx, 1998; Wilson, Beezer, and Mitchell, 1995; Yuan and Chen, 1998), temperature (Blaug and Hajratwala, 1972; Oey, Verlinde, Hendrickx, and Van Loey, 2006; Rojas and Gerschenson, 1997; Vernin, Chakib, Rogacheva, Obretenov, and Parkanyi, 1997), light (Tikekar, Anantheswaran, Elias, and LaBorde, 2011; Yang and Min, 2009), oxygen (Dhuique-Mayer et al., 2007; Eison-Perchonok and Downes, 1982; Van Bree et al., 2012), and metallic catalysts. In the presence of oxygen, AA is oxidized into DHA, which is further hydrolysed into 2,3-diketogulonic acid (DKGA) (Szultka, Buszewska-Forajta, Kaliszan, and Buszewski, 2014). The latter is very unstable and is rapidly degraded into numerous products, amongst which 3-hydroxy-2-pyrone and 2-furoic acid have been identified (Bradshaw, Barril, Clark, Prenzler, and Scollary, 2011; Yuan and Chen, 1998).

In most studies regarding ascorbic acid degradation, kinetics were modelled by means of zero-order (Laing, Schlueter, and Labuza, 1978), first-order (Burdurlu, Koca, and Karadeniz, 2006), pseudo-first order (Patkai, Kormendy, and Kormendy-Domjan, 2002; Uddin, Hawlader, Ding, and Mujumdar, 2002), or second-order (Eison-Perchonok and Downes, 1982; Singh, Heldman, and Kirk, 1976) apparent reaction models. These models were clearly described by van Boekel (2008). The first-order reaction was the most frequently reported, considering only AA as a reactant (pseudo-1rst-order), with temperature dependence described using Arrhenius' law, and identified E_a values within the range of 20–130 kJ/mol (Bosch et al., 2013; Devahastin and Niamnuy, 2010; Leskova et al., 2006). Because of the strong correlation between E_a and the pre-exponential coefficient, van Boekel (2008) and Peleg, Normand, and Corradini (2012) recommended reparametrisation of the

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Arrhenius equation by introducing a reference temperature T_{ref}, so that the pseudo-1rst-order rate constant k at a temperature T could be expressed as (Eq. (1)):

$$\frac{k}{k_{ref}} = \exp\left[\frac{-E_a}{R}\cdot\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \quad (1)$$

Few papers have considered the role of oxygen as a reactant in the ascorbic acid degradation. Two stoichiometric reactions can be found in the literature: $AA + 1/2{\cdot}O_2 \rightarrow DHA + H_2O$ and $AA + O_2 \rightarrow DHA + H_2O_2$ (Oey et al., 2006; Serpen and Gokmen, 2007; Wilson et al., 1995). Based on these studies, it can therefore be expected that the global stoichiometric coefficient for oxygen should range from 0.5 to 1 if ascorbic acid is partly degraded by both reactions. Pénicaud (2009) studied AA degradation in aqueous solutions at different temperatures (8–33 °C) and oxygen concentrations (0–21% mol/mol in the gas phase) corresponding to the storage conditions applied for foods, and fitted the kinetics using a model that was a first-order for AA and β-order for oxygen. The β values thus identified ranged from 0.6 to 1.6, depending on the temperature.

The aim of the present work was to describe the impact on the degradation of ascorbic acid and dehydroascorbic acid of both temperatures within the range of 50–90 °C (corresponding to the heat treatments that may be applied to fruit products) and oxygen concentrations within the range of 10–30% (mol/mol) in the gas phase, in order to advance the construction of a predictive model.

2. Materials and methods

2.1. Reagents

Crystalline ascorbic acid (AA) (99%), dehydroascorbic acid (DHA) 99%, DL-dithiothreitol 99%, and ethyl acetate 99.8% were purchased from Sigma-Aldrich (St. Louis, MO, USE). Malic acid, metaphosphoric acid (40–50%), *tris*(hydroxymethyl)aminomethane, and di-hydrated monobasic sodium phosphate were obtained from VWR Prolabo chemicals (Luther Worth, England). Sodium hydroxide (97%), di-hydrated dibasic sodium phosphate and hydrochloric acid 37% came from Carlo Erba (Val de Reuil, France). Water used to prepare the solutions and dilutions was purified using an ELIX system (Millipore, Bedford, MA).

2.2. Equipment

The degradation kinetics were determined using a laboratory reactor system EasyMax™ 102 (Mettler Toledo, Greifensee, Switzerland), composed of a thermostatic unit that enabled the control of temperatures between −28 and 183 °C (± 1 °C) and 100 mL-glass reactors protected from light (Fig. 1). Each reactor was equipped with a Pt100-temperature probe, a steam condenser connected to a cryostat (NESLAB RTE 300, Newington, USA), and a magnetic stirrer (set at 300 rpm). The system was operated via iControl EasyMax®4.1. The reactors were coupled to a GasMix system (AlyTech, Juvisy-sur-Orge, France) fed with pure oxygen and nitrogen, enabling a supply of gas at the desired oxygen concentration (accurate to ± 2%) that was bubbled in the liquid phase in the reactor just above the stirrer and during all the kinetics with a continuous flowrate of 500NmL/min.

When evaluating the performance of the reactor, account was taken of its ability to achieve and maintain temperature over a given period of time. The temperature probes were calibrated within the range 0–100 °C using a certified oven (WIKA CTD 91000-450 N°581003, Klingenberg, Germany) connected to a Testo 735-1 measuring chain (Forbach, France). The consistency of temperature determinations over time was assessed by calculating the time-related variation coefficient for each temperature point (50, 60, 70, 80, 85, and 90 °C), recorded every 2 s. The coefficients of variation did not exceed 0.5%, indicating that no significant variations in temperature occurred during the kinetics. The oxygen concentration supplied by the GasMix device was verified by measuring the partial pressure in oxygen in the solution and headspace using a Fibox 3LCD Trace V7 oxygen meter (PreSens, Regensburg, Germany). Because this device was limited to temperatures < 50 °C, the oxygen partial pressures were systematically measured at 25 °C before heating was started and assumed to be the same at higher temperatures. The quantity of dissolved oxygen is then calculated with Henry's law. Previous experiments were done with a gas flowrate of 1000NmL/min under the same agitation and showed no difference in the degradation kinetic of ascorbic acid. It can thus be assumed that the oxygen content of the liquid phase is constant all over the experiment.

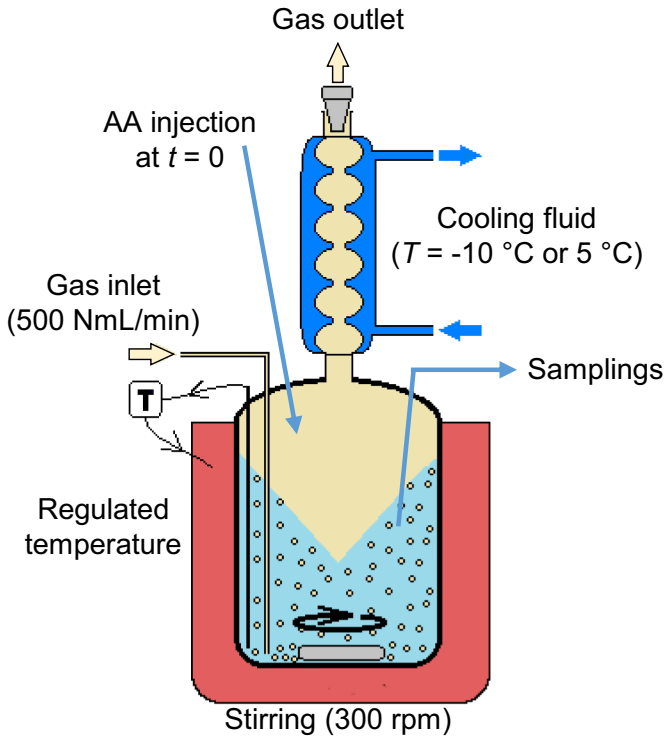

Fig. 1. Schematic representation of the reactor used for the kinetics.

Thanks to the high level of agitation, the continuous bubbling at a high flowrate, and the thermostatic unit covering all the reactor (except for the cover), the content of the reactor was assumed to be perfectly stirred, with constant temperature and dissolved oxygen concentration.

2.3. Experimental kinetics

The degradation kinetics of ascorbic acid were determined at six different temperatures (50, 60, 70, 80, 85, and 90 °C) and at three different concentrations of oxygen in the gas phase (10, 21 and 30% mol/mol). Each kinetic determination was repeated at least twice, and a maximum of nine times (i.e. $n = 2$ to 9).

The initial concentration in ascorbic acid was set at 5.6 mM or 1 g/L. This was achieved by adding 5 mL of a stock solution of ascorbic acid (around 112 mM or 20 g/L) to 95 mL of 20 mM malate buffer at pH 3.8 (adjusted using a 5 M sodium hydroxide solution). The buffer solution, under continuous stirring and gas bubbling, was preheated and equilibrated at the chosen oxygen partial pressure for at least 30 min before adding the AA. Samples of 1.5 mL were removed regularly to measure the AA and DHA concentrations. The duration varied with temperature and was chosen to achieve at least 70% of degradation of ascorbic acid (as advised by van Boekel, 2008).