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

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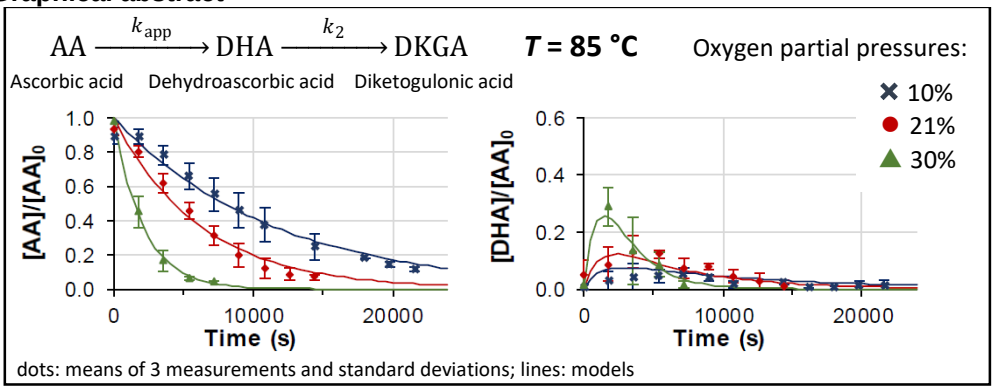
Abstract
The degradation kinetics of vitamin C (ascorbic and dehydroascorbic acids, AA and DHA) were determined under controlled conditions of temperature (50 - 90 °C) and oxygen concentrations in the gas phase (10 - 30% mol/mol) using a specific reactor. The degradation of vitamin C in malate buffer (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.

Key words: vitamin C, oxidation, oxygen partial pressure, kinetic rate constants.

Graphical abstract



Highlights

- Ascorbic acid degradation is increased by temperature and oxygen concentration
- Dehydroascorbic acid degradation is increased by temperature
- Experimental data on AA and DHA were well fitted using first order kinetic models
- Apparent kinetic rate constants for AA degradation do not follow Arrhenius' law
- Oxygen stoichiometry appears to be temperature-dependent

Chemical compounds studied in this article:
Ascorbic acid (PubChem CID: 54670067); Dehydroascorbic acid (PubChem CID: 440667).

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, & Vikram, 2009; Shashirekha, Mallikarjuna, & Rajarathnam, 2015). Vitamin C acts as an antioxidant, having a potentially protective role against cardiovascular diseases and certain cancers (Block, 1991; Frei, Birlouez-Aragon, & 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 & Lloyd, 2012). AA is a quite unstable compound and its degradation is closely dependent on environmental conditions such as pH (Golubitskii, Budko, Basova, Kostarnoi, & Ivanov, 2007; Van den Broeck, Ludikhuyze, Weemaes, Van Loey, & Hendrickxx, 1998; Wilson, Beezer, & Mitchell, 1995; Yuan & Chen, 1998), temperature (Blaug & Hajratwala, 1972; Oey, Verlinde, Hendrickx, & Van Loey, 2006; Rojas & Gerschenson, 1997; Vernin, Chakib, Rogacheva, Obretenov, & Parkanyi, 1997), light (Tikekar, Anantheswaran, Elias, & LaBorde, 2011; Yang & Min, 2009), oxygen (Dhuique-Mayer, Tbatou, Carail, Caris-Veyrat, Dornier, & Amiot, 2007; Eison-Perchonok & Downes, 1982; Van Bree, Baetens, Samapundo, Devlieghere, Laleman, Vandekinderen, 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, & 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, & Scollary, 2011; Yuan & Chen, 1998).

In most studies regarding ascorbic acid degradation, kinetics were modelled by means of zero-order (Laing, Schlueter, & Labuza, 1978), first-order (Burdurlu, Koca, & Karadeniz, 2006), pseudo-first order (Patkai, Kormendy, & Kormendy-Domjan, 2002; Uddin, Hawlader, Ding, & Mujumdar, 2002), or second-order (Eison-Perchonok & Downes, 1982; Singh, Heldman, & 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-1^{rst}-order), with temperature dependence described using Arrhenius' law, and identified E_a values within the range of 20-130 kJ/mol (Bosch, Cilla, Garcia-Llatas, Gilabert, Boix, & Alegria, 2013; Devahastin & Niamnuy, 2010; Leskova, Kubikova, Kovacikova, Kosicka, Porubska, & Holcikova, 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 Arrhenius equation by introducing a reference temperature T_{ref}, so that the pseudo-1^{rst}-order rate constant k at a temperature T could be expressed as (Eq. 1):

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

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 + ½ · O_2 → DHA + H_2O and AA + O_2 → DHA + H_2O_2 (Oey, et al., 2006; Serpen & 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 500 NmL/min.

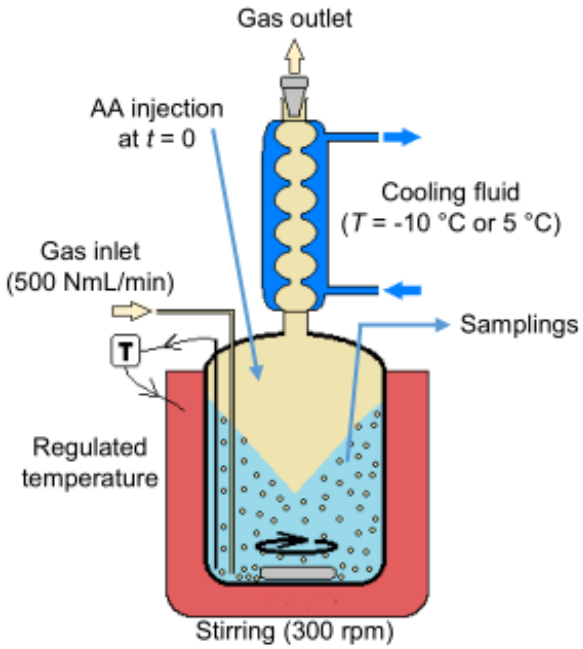


Fig. 1. Schematic representation of the reactor used for the kinetics.

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 1000 NmL/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.
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).

2.4 Quantification of ascorbic and dehydroascorbic acids

An indirect spectrophotometric measurement method was used to quantify both ascorbic and dehydroascorbic acids (Gómez Ruiz, Roux, Courtois, & Bonazzi, 2016). 0.5 mL of a solution containing both AA and DHA was sampled from the reactor and diluted to 1/50 (v/v) in a stopping solution of 3% (m/v) metaphosphoric acid (MPA). Absorbance (A) was read at 243 nm against a blank containing malate buffer (20 mM pH 3.8) on a Specord 210 Plus spectrophotometer (Analytik Jena AG, Jena, Germany). This absorbance was then converted into an ascorbic acid concentration before correction for the evaporated volume ($[AA]_{bcv}$) using a calibration curve (Eq. 2):

$$A = 0.2135 \cdot [\mathrm{AA}]_{\mathrm{bcv}} + 0.0292 \quad (2)$$

In parallel, in order to reduce DHA in AA, a 0.5 mL sample was mixed with 0.5 mL of a 30 mM DL-dithiothreitol (DTT) solution prepared in 0.1 mM phosphate buffer pH 7.5 and 1 mL 0.2 M tris HCl buffer pH 8.2, and placed in an ice bath in the dark. After 30 min, the excess DTT was eliminated by three successive extractions with ethyl acetate. The reduced sample was then treated in the same way as the initial sample and the second absorbance value (A_{total}) was converted into a second concentration in AA which corresponded to both native AA and reduced DHA ([AA+DHA]), using Eq. 2. The initial AA concentration was then deduced to obtain a DHA concentration before correction for regression ($[DHA]_{bcr}$). This concentration had to be corrected to give the actual DHA concentration before correction for the evaporated volume ($[DHA]_{bcv}$) using Eq. 3, as proposed by Gómez Ruiz, et al. (2016):

$$[DHA]_{\mathrm{bcv}} = \left([DHA]_{\mathrm{bcr}} \cdot \frac{1}{0.7524}\right) - (1.014 \cdot A_{\mathrm{total}} + 0.1529) \quad (3)$$

To establish the kinetics, the real volume of the batch at each sampling time had to be recalculated while taking account of evaporation and previous sampling, using Eq. 4 for AA. The same equation was then used for DHA by replacing $[AA]_t$ and $[AA]_{bcv}$ by $[DHA]_t$ and $[DHA]_{bcv}$, respectively.

$$[\mathrm{AA}]_t = \frac{[\mathrm{AA}]_{\mathrm{bcv}} \cdot \left(V_0 - (V_e)_t - \sum_0^{i-1} V_s\right)}{\left(V_0 - \sum_0^{i-1} V_s\right)} \quad (4)$$

where $[AA]_t$ is the true concentration in ascorbic acid at time t, $[AA]_{bcv}$ the concentration before correction for the evaporated volume calculated from the calibration curve, V_0 the initial volume of the reactor, $(V_e)_t$ the evaporated volume at time t and $\sum_0^{i-1} V_s$ the cumulated sampled volume up to i-1 sampling. The evaporated volume at time t was calculated from the initial and final volumes in the reactor, assuming that evaporation occurs under a steady-state regime.

2.5 Determination of dissolved oxygen concentrations

Determination of the oxygen concentration dissolved in the liquid medium was based on Henry's law (Eq. 5) linking the partial pressure in oxygen calculated from the percentage in oxygen as imposed by the GasMix device (Eq. 6) and Henry's constant (H_{O2}). Winkler's table gives the dissolved oxygen concentration in pure water for 21% (mol/mol) oxygen in the gas phase in equilibrium with the liquid phase at different temperatures (Winkler, 1888), and makes it possible to calculate H_{O2} using Eq. 5. As H_{O2} is only dependent on temperature, then any other oxygen percentage can be processed using the previously determined H_{O2} values and Eqs. 5 and 6, assuming that the malate buffer (20 mM, pH 3.8) used here can be assimilated to pure water due to its low concentration.

$$[O_2] = \frac{p_{O2} \cdot H_{O2}}{M_{O2}} \quad (5)$$

$$p_{O2} = \frac{\%O_2}{100} \cdot P_{atm} \quad (6)$$

where $[O_2]$ is the concentration of dissolved oxygen in the liquid medium (M), p_{O2} the partial pressure of oxygen (Pa), H_{O2} Henry's constant which varies in line with gas, temperature and liquid (g/L/Pa), M_{O2} the molecular mass of oxygen (g/mol), $\%O_2$ the percentage of oxygen (mol/mol) in the gas, and P_{atm} the atmospheric pressure (Pa).

2.6 Data processing

The data were processed using Microsoft Excel®. The solver was used to determine the unknown parameters of the models by minimising the sum of the squares (*SS*) between experimental and predicted data (Eq. 7). A complementary macro called SolverAid (de Levie, 2012) was used to calculate the standard deviation on identified parameters and adjustments.

$$SS = \sum_1^N ((y_i - \hat{y}_i)^2) \quad (7)$$

where y_i are the experimental values, $\hat{y}_i$ the predicted values and *N* the number of experimental values. The relative root mean square error (*RMSE*) was then used to evaluate the quality of fit.

$$RMSE = \frac{1}{\bar{\hat{y}}} \cdot \sqrt{\frac{\sum_1^N ((y_i - \hat{y}_i)^2)}{N}} \quad (8)$$

where $\bar{\hat{y}}$ is the mean of the predicted values.

3. Results and discussion

3.1 Kinetics of ascorbic and dehydroascorbic acid degradation

Ascorbic acid degradation kinetics (Fig. 2) displayed an exponential behaviour consistent with a first order reaction as classically described in the literature. Dehydroascorbic acid kinetics exhibited an increasing phase followed by a decreasing one, which was consistent with it being an intermediate product, sequentially formed and degraded. The repeatability of the experiments, evaluated by comparing three sets of data acquired under each experimental condition, is quite satisfactory. However, a shift between curves may have been due to a difference in initial AA contents which it was impossible to measure because of the time required for homogenisation after addition of the stock solution containing AA at $t = 0$. The values need to be corrected by calculating the ratio between AA and DHA concentrations at any time and AA concentration at the initial time ($[AA]/[AA]_0$ and $[DHA]/[AA]_0$). $[AA]_0$ was identified by an exponential smoothing of the experimental data (supplementary material). After this standardization step, all kinetics varies between 1 and 0 and can then be treated all together as repetitions. Results confirmed the good repeatability as standard deviations were quite low for AA (mean coefficient of variation of 16%) but higher for DHA (mean CV of 47%) because of the lower measured values (Fig. 3).

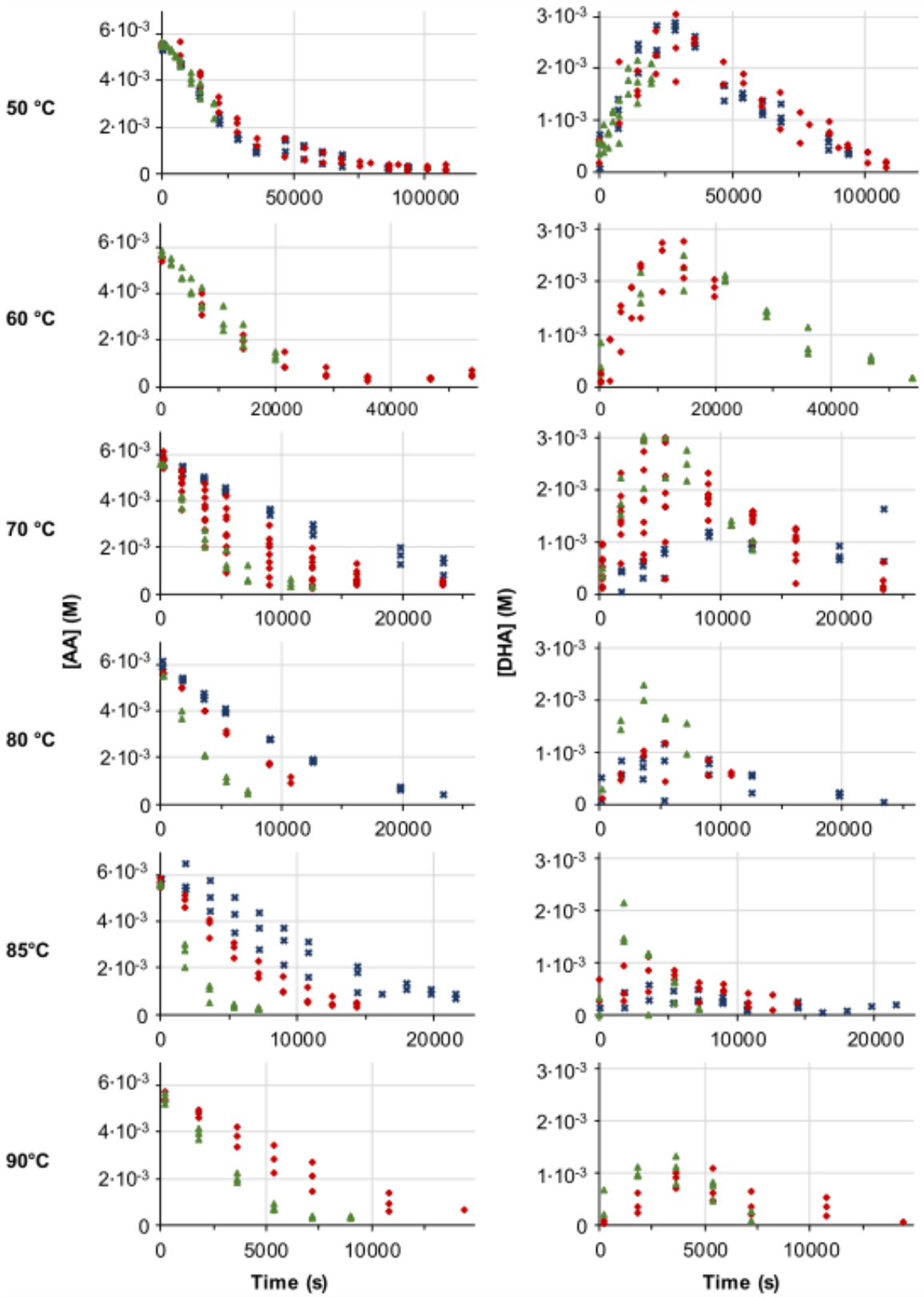


Fig. 2. Kinetics of ascorbic acid (left) and dehydroascorbic acid (right) contents during AA degradation experiments at six temperatures and three oxygen concentrations in the gas phase: ✖ 10%; ● 21%; ▲ 30% mol/mol. Each kinetics was repeated between 2 and 9 times. All experimental points are shown.

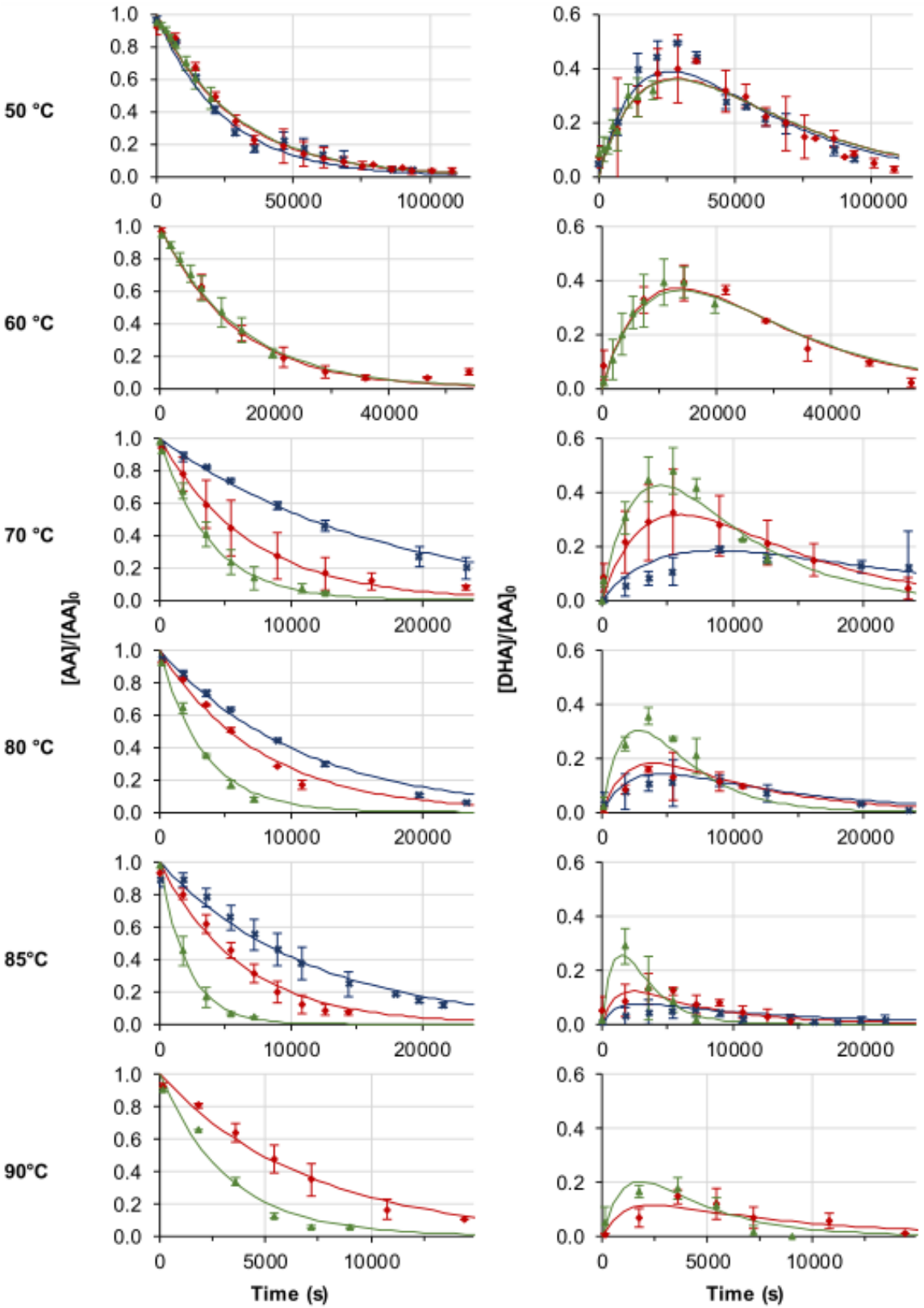


Fig. 3. Apparent kinetic models (—) (Eqs. 11 and 12) and experimental data (mean and standard deviation, n = 2-9) for six temperatures and three oxygen concentrations in the gas phase (✖ 10%; ● 21%; ▲ 30% mol/mol), with respect to standardised ascorbic acid (left) and dehydroascorbic acid (right) concentrations.

As expected, the degradation reaction was enhanced by the temperature. The impact of oxygen depends on the temperature range. Increasing the partial pressure seems to have no effect on AA degradation at low temperatures (50 and 60 °C) but a significant one at higher temperatures (70 to 90 °C) leading to lower remaining ascorbic acid contents. This different behaviour regarding oxygen has not been reported in previous studies where increasing the dissolved oxygen concentration increased the kinetic rate constant even at low temperatures (Eison-Perchonok & Downes, 1982; Pénicaud, Bohuon, Peyron, Gontard, & Guillard, 2012). Conclusion concerning the effect of temperature and oxygen on DHA behaviour are difficult to draw at this stage because of the two consecutive reactions involved (formation of DHA from AA and degradation of DHA to further products), both potentially depending on temperature.

3.2 Apparent model for the degradation of ascorbic and dehydroascorbic acids

In order to model AA and DHA degradation kinetics using an apparent model, a very simple reaction scheme was considered first of all:

$$\mathrm{AA} \xrightarrow{k_{\mathrm{app}}} \mathrm{DHA} \xrightarrow{k_2} \mathrm{DKGA}$$

AA is degraded into DHA with a kinetic rate constant k_{app} as a function of dissolved oxygen concentration and temperature, and DHA is degraded into other products with a kinetic rate constant k_2 as a function of temperature. The rates of AA and DHA degradation can then be written, using first order reactions as given by the reaction involving one molecule of compound at each step (Eqs. 9 and 10):

$$\frac{d[\mathrm{AA}]}{dt} = -k_{\mathrm{app}} \cdot [\mathrm{AA}] \quad (9)$$

$$\frac{d[\mathrm{DHA}]}{dt} = k_{\mathrm{app}} \cdot [\mathrm{AA}] - k_2 \cdot [\mathrm{DHA}] \quad (10)$$

Both equations can be solved analytically, assuming constant temperature and dissolved oxygen concentration, to give variations in AA and DHA concentrations over time (Eqs. 11 and 12):

$$\frac{[\mathrm{AA}]_t}{[\mathrm{AA}]_0} = \exp\left(-k_{\mathrm{app}} \cdot t\right) \quad (11)$$

$$\frac{[\mathrm{DHA}]_t}{[\mathrm{AA}]_0} = \frac{k_{\mathrm{app}}}{k_2 - k_{\mathrm{app}}} \cdot \left(\exp\left(-k_{\mathrm{app}} \cdot t\right) - \exp(-k_2 \cdot t)\right) + \frac{[\mathrm{DHA}]_0}{[\mathrm{AA}]_0} \cdot \exp(-k_2 \cdot t) \quad (12)$$

To use both equations for $[AA]_t$ and $[DHA]_t$ prediction, $[AA]_0$ was set at 1, as the work was performed on standardized data, and $[DHA]_0$ at 0.

For each experimental condition (six temperatures and three oxygen partial pressures), the apparent kinetic rate constants of AA degradation (k_{app}) and DHA degradation (k_2), were identified by minimising the difference between the experimental data and the model. The calculations confirmed that k_2 values were not significantly affected by oxygen, as similar values were obtained for each partial pressure at the same temperature. Identifications were then performed for one k_2 value per temperature, while k_{app} values also depended on oxygen (Table 1). No correlation between k_{app} and k_2 appeared during this identification process. The values obtained confirmed that this apparent first order model (Eqs. 11 and 12) was efficient in fitting to the experimental data (Fig. 3). *RMSE* calculated on AA kinetics were satisfactory, ranging from 7% to 19%, but higher for DHA kinetics (from 25% to 60%) because of the greater dispersion of experimental points and the lower values of DHA concentrations. However, the models (Eqs. 11 and 12) appeared to fit adequately with the experimental data.

The k_{app} values identified (Table 1) increased in line with temperature (from $3.5 \cdot 10^{-5}$ s^{-1} at 50 °C to $4.8 \cdot 10^{-4}$ s^{-1} at 85 °C) and with the oxygen partial pressures (for example, at 85 °C from $8.9 \cdot 10^{-5}$ s^{-1} at 10% to $4.8 \cdot 10^{-4}$ s^{-1} at 30%). However, the lack of a link to the oxygen content for the kinetics at 50 and 60 °C was confirmed, with identical k_{app} values being obtained for each partial pressure. Pénicaud, et al. (2012) had noted differences at 20 °C between the kinetics, with 0.028 and 0.289 mM dissolved oxygen, obtaining k_{app} values of $1.9 \cdot 10^{-7}$ and $1.4 \cdot 10^{-6}$ s^{-1}, respectively. Eison-Perchonok and Downes (1982) also observed significant differences in k_{app} values according to the oxygen percentage, with values ranging from 1.7 s^{-1}

for 10% to 3.5 s^{-1} for 21% at 50 °C and from 2.0 s^{-1} for 10% to 3.4 s^{-1} for 15% at 55 °C. In addition, the k_{app} values found during the present study were much lower than those previously identified by other authors under comparable conditions. But the findings in the literature have been contradictory. For example, Blaug and Hajratwala (1972), who worked in closed containers with headspace, found values lower than Rojas and Gerschenson (1997), who worked in closed containers without headspace (k_{app} values at 80 °C equal to 0.11 s^{-1} and 1.4 s^{-1}, respectively) at the same pH of 3.5, but both values were very high when compared to those we found (k_{app} at 80 °C and 21% O_2 equals $1.3 \cdot 10^{-4}$ s^{-1}). Eison-Perchonok and Downes (1982) found even higher values, with k_{app} at 50 °C and 21% O_2 being 3.5 s^{-1}, but in their case the pH was higher (6.1) and studies have shown that raising the pH will increase the value of the kinetic rate constant (Rojas & Gerschenson, 1997; Van den Broeck, et al., 1998; Wilson, et al., 1995). Only the value found by Pénicaud, et al. (2012) appeared to be in the same order of magnitude as those identified here, with a k_{app} value of $1.4 \cdot 10^{-6}$ s^{-1} at 20 °C and 21% of oxygen.

Table 1. Kinetic parameters identified for the apparent first order modelling of AA and DHA degradation and model adjustment

T (°C)	O_2 (% mol/mol) in the gas	$[O_2]$ (M) in the liquid	k_{app} (s^{-1}) (mean ± s.d.)	k_2 (s^{-1}) (mean ± s.d.)	*RMSE* (%) AA	DHA
50	10	$8.18 \cdot 10^{-5}$	$4.06 \cdot 10^{-5} \pm 0.14 \cdot 10^{-5}$	$3.61 \cdot 10^{-5} \pm 0.12 \cdot 10^{-5}$	12.1	30.3
	21	$1.72 \cdot 10^{-4}$	$3.51 \cdot 10^{-5} \pm 0.12 \cdot 10^{-5}$			
	30	$2.46 \cdot 10^{-4}$	$3.46 \cdot 10^{-5} \pm 0.16 \cdot 10^{-5}$			
60	21	$1.47 \cdot 10^{-4}$	$7.47 \cdot 10^{-5} \pm 0.31 \cdot 10^{-5}$	$7.34 \cdot 10^{-5} \pm 0.36 \cdot 10^{-5}$	11.1	24.7
	30	$2.09 \cdot 10^{-4}$	$7.19 \cdot 10^{-5} \pm 0.25 \cdot 10^{-5}$			
70	10	$5.67 \cdot 10^{-5}$	$0.61 \cdot 10^{-4} \pm 0.04 \cdot 10^{-4}$	$1.94 \cdot 10^{-4} \pm 0.10 \cdot 10^{-4}$	18.8	43.6
	21	$1.19 \cdot 10^{-4}$	$1.46 \cdot 10^{-4} \pm 0.05 \cdot 10^{-4}$			
	30	$1.70 \cdot 10^{-4}$	$2.63 \cdot 10^{-4} \pm 0.18 \cdot 10^{-4}$			
80	10	$4.18 \cdot 10^{-5}$	$0.93 \cdot 10^{-4} \pm 0.03 \cdot 10^{-4}$	$4.30 \cdot 10^{-4} \pm 0.24 \cdot 10^{-4}$	7.0	36.7
	21	$8.78 \cdot 10^{-5}$	$1.31 \cdot 10^{-4} \pm 0.05 \cdot 10^{-4}$			
	30	$1.25 \cdot 10^{-4}$	$2.97 \cdot 10^{-4} \pm 0.13 \cdot 10^{-4}$			
85	10	$3.33 \cdot 10^{-5}$	$0.89 \cdot 10^{-4} \pm 0.03 \cdot 10^{-4}$	$9.20 \cdot 10^{-4} \pm 0.74 \cdot 10^{-4}$	14.6	64.8
	21	$7.00 \cdot 10^{-5}$	$1.62 \cdot 10^{-4} \pm 0.06 \cdot 10^{-4}$			
	30	$1.00 \cdot 10^{-4}$	$4.77 \cdot 10^{-4} \pm 0.27 \cdot 10^{-4}$			
90	21	$4.97 \cdot 10^{-5}$	$1.43 \cdot 10^{-4} \pm 0.06 \cdot 10^{-4}$	$8.83 \cdot 10^{-4} \pm 0.80 \cdot 10^{-4}$	12.6	46.7
	30	$7.10 \cdot 10^{-5}$	$3.13 \cdot 10^{-4} \pm 0.14 \cdot 10^{-4}$			

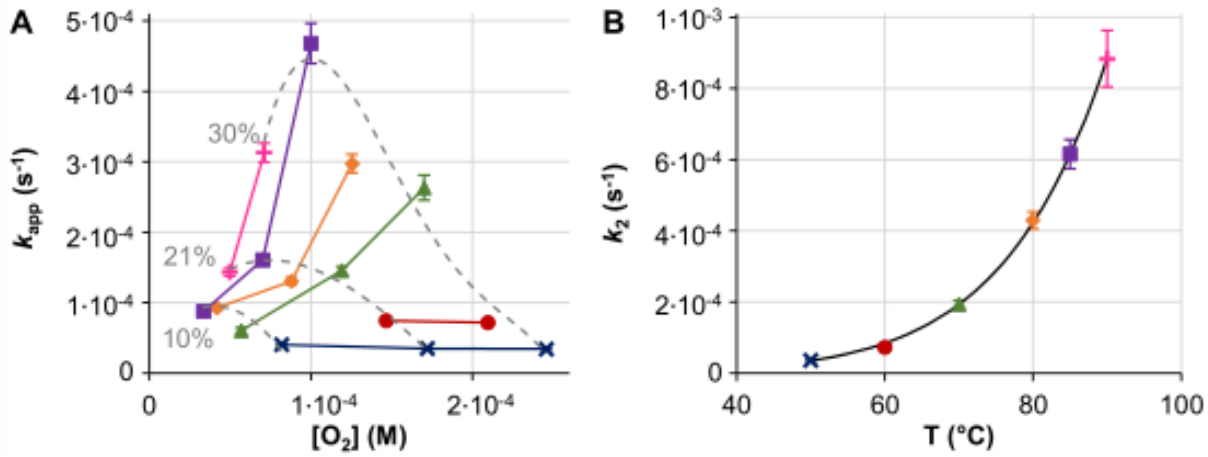


Fig. 4. Kinetic rate constants of ascorbic acid degradation (k_{app}) as a function of temperature and dissolved oxygen concentrations (A) and dehydroascorbic acid degradation (k_2) as a function of temperature (B), at six temperatures (✕ 50 °C; ● 60 °C; ▲ 70 °C; ◆ 80 °C; ■ 85 °C; ✚ 90 °C). Grey dotted lines (**- -**) trace the behaviour of k_{app} at iso-oxygen concentrations in the gas phase (10%, 21% and 30% mol/mol). The black line (—) is the Arrhenius model (Eq. 1) fitted to experimental k_2 values.

Plotting identified k_{app} values as a function of the dissolved oxygen concentration (Fig. 4A) highlighted the limitations of this apparent modelling, with lower k_{app} at 90 °C than at 85 °C under the same oxygen partial pressure, thus contradicting the generally accepted principle of Arrhenius' law. In fact, increasing the temperature also meant decreasing the concentration of oxygen dissolved in the medium for an identical partial pressure (Eq. 5) and it appears that above a certain value, a rise in temperature was not sufficient to compensate for the depletion of oxygen, leading to a lowering of the value of the apparent kinetic rate constant. On the other hand, k_2 values for the different temperatures indeed followed Arrhenius' law (Fig. 4B), making possible to identify $k_{ref} = 1.94 \cdot 10^{-4} \pm 0.04 \cdot 10^{-4}$ s^{-1} (T_{ref} = 70 °C) and E_a = 78.7 ± 1.2 kJ/mol. However, confidence in this result was poor because of the small number of data available (only six temperatures), leading to a strong correlation between the two parameters (correlation coefficient of -0.96).

3.3 Model including oxygen dependence to determine ascorbic acid degradation

For an oxidative reaction such as ascorbic acid degradation, the oxygen concentration must be taken into account when calculating the real kinetic rate constant based on the stoichiometry of the reaction, which in the present case is unknown:

$$AA + \beta \cdot O_2 \overset{k_1}{\rightarrow} DHA \overset{k_2}{\rightarrow} DKGA$$

Such a formulation of the reaction is perhaps excessive as the reactions are not equilibrated because of the $2 \cdot \beta$ moles of oxygen and the 2 moles of hydrogen that "disappear" between the first and second steps. However, this formulation enables oxygen to appear as a reactant in the reaction scheme and thus in the differential equations (Eqs. 13 and 14):

$$\frac{d[\mathrm{AA}]}{dt} = -k_1 \cdot [\mathrm{O_2}]^{\beta} \cdot [\mathrm{AA}] \quad (13)$$

$$\frac{d[\mathrm{DHA}]}{dt} = k_1 \cdot [\mathrm{O_2}]^{\beta} \cdot [\mathrm{AA}] - k_2 \cdot [\mathrm{DHA}] \quad (14)$$

These equations can be solved analytically, knowing that the temperature and dissolved oxygen concentration are maintained constant throughout the experiment, to produce other expressions of AA and DHA behaviour over time (Eqs. 15 and 16):

$$\frac{[\mathrm{AA}]_t}{[\mathrm{AA}]_0} = \exp\left(-k_1 \cdot [\mathrm{O_2}]^{\beta} \cdot t\right) \quad (15)$$

$$\frac{[\mathrm{DHA}]_t}{[\mathrm{AA}]_0} = \frac{k_1 \cdot [\mathrm{O_2}]^{\beta}}{k_2 - k_1 \cdot [\mathrm{O_2}]^{\beta}} \cdot \left(\exp\left(-k_1 \cdot [\mathrm{O_2}]^{\beta} \cdot t\right) - \exp(-k_2 \cdot t)\right) + \frac{[\mathrm{DHA}]_0}{[\mathrm{AA}]_0} \cdot \exp(-k_2 \cdot t) \quad (16)$$

Another time, to use both equations for $[AA]_t$ and $[DHA]_t$ prediction, $[AA]_0$ was set at 1, as the work was performed on standardized data, and $[DHA]_0$ at 0.

Determination of the actual kinetic rate constant (k_1) must be performed concomitantly with the stoichiometric coefficient (β), as none is clearly known. Initial tests showed that no single β value could be identified for all temperatures as the oxygen dependence appeared to be null at 50 °C and clearly visible at higher temperatures. An identification was performed regarding the Arrhenius parameters (k_{ref} and E_a) of the two reactions and the six β coefficients corresponding to the six different temperatures (Table 2). The results showed that the values identified for the ten parameters were consistent with the expected behaviour and very similar (regarding the second reaction) to those identified previously ($k_{2ref} = 1.94 \cdot 10^{-4}$ and $2.01 \cdot 10^{-4}$ s^{-1} and E_{a2} = 78.7 and 82.5 kJ/mol, respectively). Despite the large quantity of experimental data available, the parameters identified concerning reaction 1 remained strongly correlated (> 0.99), which questions the meaning of the values identified. The β values did not range from 0.5 to 1, as could have been expected from the literature. This was also the case during the study by Pénicaud (2009) where β values ranged from 0.6 to 1.6 (for temperatures between 8 and 33 °C). Nevertheless, the two studies exhibited uncoherent results, as, according to our β values versus temperature, we would have obtained β values of 0 for temperatures lower than 50 °C.

Table 2. Identification results of three different trials: Identification 1 designed to determine the Arrhenius parameters of the two reactions and one β value per temperature; Identification 2 designed to determine the Arrhenius parameters and the two coefficients of a linear shape of $\beta(T)$ in order to resolve correlation problems by minimising the number of parameters to be identified; and Identification 3, which was the same as the previous one but used a quadratic shape for $\beta(T)$.

	Identification 1	Identification 2	Identification 3
Identified parameters (mean ± s.d.)			
Arrhenius parameters (T_{ref} = 70 °C)			
k_{1ref} ($L^{\beta}/mol^{\beta}/s$)	$2.02 \cdot 10^{-1} \pm 0.06 \cdot 10^{-1}$	$2.06 \cdot 10^{-2} \pm 0.07 \cdot 10^{-2}$	$1.65 \cdot 10^{-1} \pm 0.05 \cdot 10^{-3}$
E_{a1} (J/mol)	$3.97 \cdot 10^{5} \pm 0.01 \cdot 10^{5}$	$3.00 \cdot 10^{5} \pm 0.02 \cdot 10^{5}$	$3.89 \cdot 10^{5} \pm 0.02 \cdot 10^{3}$
k_{2ref} (s^{-1})	$2.01 \cdot 10^{-4} \pm 0.01 \cdot 10^{-4}$	$2.04 \cdot 10^{-4} \pm 0.01 \cdot 10^{-4}$	$2.01 \cdot 10^{-4} \pm 0.01 \cdot 10^{-7}$
E_{a2} (J/mol)	$8.25 \cdot 10^{4} \pm 0.02 \cdot 10^{4}$	$8.32 \cdot 10^{4} \pm 0.03 \cdot 10^{4}$	$8.23 \cdot 10^{4} \pm 0.02 \cdot 10^{2}$
$\beta(T)$		$\beta = a_0 + a_1 \cdot T$	$\beta = a_0 + a_1 \cdot T + a_2 \cdot T^2$
$\beta_{(50)}$	0.000 ± 0.000	a_0 $-1.36 \cdot 10^{0} \pm 0.01 \cdot 10^{0}$	a_0 $-2.49 \cdot 10^{0} \pm 0.02 \cdot 10^{0}$
$\beta_{(60)}$	0.434 ± 0.002	a_1 $2.71 \cdot 10^{-2} \pm 0.02 \cdot 10^{-2}$	a_1 $5.74 \cdot 10^{-2} \pm 0.05 \cdot 10^{-2}$
$\beta_{(70)}$	0.801 ± 0.003		a_2 $-1.50 \cdot 10^{-4} \pm 0.02 \cdot 10^{-4}$
$\beta_{(80)}$	1.170 ± 0.005		
$\beta_{(85)}$	1.325 ± 0.005		
$\beta_{(90)}$	1.493 ± 0.006		
Parameters correlation [a]			
	k_{1ref} / E_{a1} 0.995	E_{a1} / a_0 -0.942	E_{a1} / a_0 -0.972
	k_{1ref} / all β > 0.99 [b]	E_{a1} / a_1 0.996	E_{a1} / a_1 0.950
	E_{a1} / all β > 0.99 [b]	a_0 / a_1 -0.963	a_0 / a_1 -0.976
	β / β > 0.99 [b]		a_1 / a_2 -0.937
Adjustment results			
RMSE AA (%)	17.1	19.9	17.2
RMSE DHA (%)	42.0	45.1	42.8
Remarks			
	$\beta = f(T)$ linear R^2 = 0.9977; quadratic R^2 = 0.9998	unacceptable adjustment and still correlation problems	acceptable adjustment but still correlation problems

[a] only correlations higher than 0.5 are shown.

[b] except for correlations with $\beta_{(50)}$ whose values are not calculable ($\beta_{(50)}$ equals 0) and for correlations with $\beta_{(60)}$ whose values are around 0.96.

Regarding the oxidation reaction transforming AA into DHA, one hypothesis is that only a proportion of the oxygen is active during the reaction in order to scavenge the two electrons released by AA. Thus the β coefficient calculated here may have represented both the "real" stoichiometric coefficient applied to the activated form of oxygen (independent of temperature) and the ratio between the activated and molecular oxygen concentrations (probably dependent on temperature). Activated oxygen may be formed by the Fenton reaction because of traces of metal in the matrix (Bradshaw, et al., 2011).

The results obtained for β could be linked to temperature using a linear ($\beta = -1.82 + 3.71 \cdot 10^{-2} \cdot T$; $R^2 = 0.9977$) or quadratic ($\beta = -2.56 + 5.93 \cdot 10^{-2} \cdot T - 1.58 \cdot 10^{-4} \cdot T^2$; $R^2 = 0.9998$) regression. New parameters were then identified by replacing the six β values with only two values for the linear coefficients (Identification 2) or three values for the quadratic coefficients (Identification 3) (Table 2). The new Arrhenius parameters identified were very close to the previous ones. The correlation results were lower in both cases. However, the model adjustment was not acceptable with respect to the linear regression (Identification 2).

Even though the *RMSE* values did not differ markedly from the initial ones (19.9% versus 17.1% and 45.1% versus 42.0% for AA and DHA, respectively), the model was significantly less adequate and did not well describe the impact of oxygen at the different temperatures. However, using the quadratic model (Identification 3), the *RMSE*s were almost the same and the model did not differ visually from the original model. It appears that the model was highly sensitive to the β values, as the small difference in fit between the linear and quadratic models was sufficient to significantly affect the adjustment results. Problems of correlation between the parameters, mostly affecting the quadratic regression coefficients and the activation energy of reaction 1, still remained but to a lesser extent. This correlation problem is hard to solve as the problem is due to the power-law shape of the model. Some authors have worked on reparametrisation methods in order to transform the structure of the equation, as it is now frequently done on the Arrhenius equation to resolve parameter correlation issues (Schwaab, Lemos, & Pinto, 2008; Schwaab & Pinto, 2007). They found a methodology that could transform the power law into a simple function but this does not seem to be appropriate for complex models involving several additive terms in an equation and also coupled differential equations (Schwaab & Pinto, 2008). Due to this mathematical complexity, an option could be to focus further work on identifying the form of oxygen which is really active in the reaction scheme in order to have a unique β value to identify.

4. Conclusion

This work demonstrated the effects of temperature and dissolved oxygen concentrations on the behaviour of ascorbic and dehydroascorbic acids in a liquid medium. The degradation of AA increased in line with temperature and could successfully be described using a first order apparent kinetic model under all the temperature and oxygen conditions studied. The degradation of DHA appeared to depend on temperature but not on oxygen concentration, as could be anticipated in view of the reaction pathway, being well described by a first order reaction and identified kinetic rate constants that adequately followed Arrhenius' law. However, although this apparent model produced a good simulation of AA and DHA behaviour over time, it was not sufficient to explain the oxygen dependence of AA degradation. Indeed, a marked dependence of the reaction on the dissolved oxygen content was found and this needs to be taken into account in the model. In this way, a more realistic kinetic rate constant (k_1) could be calculated and not only an apparent kinetic rate constant (k_{app}) dependent on the oxygen concentration. Related to this k_1, the stoichiometric coefficient of oxygen (β) also needs to be identified. However, some limitations were seen during the identification process, regarding strongly coupled parameters. Attempts made to overcome this coupling by using a quadratic regression for $\beta(T)$ were able to alleviate this problem but not completely resolve it. Further studies now need to better explore the reaction pathways of AA degradation in order to enrich the model with new reactions and determine whether it is possible to improve the performance of the model and enable its more widespread use.

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Supplementary material - Parameters (mean ± s.d.) of the exponential models ($[AA] = [AA]_0 \cdot \exp(-k \cdot t)$) used on the raw data of ascorbic acid

T (°C)	P_{O2} (%)	Repetition	$[AA]_0$ (M)	k (s^{-1})	*RMSE* (%)
50	10	1	$5.71 \cdot 10^{-3} \pm 0.23 \cdot 10^{-3}$	$4.15 \cdot 10^{-5} \pm 2.88 \cdot 10^{-6}$	14.30
		2	$5.52 \cdot 10^{-3} \pm 0.30 \cdot 10^{-3}$	$3.66 \cdot 10^{-5} \pm 3.43 \cdot 10^{-6}$	18.22
		3	$5.72 \cdot 10^{-3} \pm 0.25 \cdot 10^{-3}$	$3.50 \cdot 10^{-5} \pm 2.58 \cdot 10^{-6}$	14.05
50	21	1	$6.42 \cdot 10^{-3} \pm 0.31 \cdot 10^{-3}$	$3.47 \cdot 10^{-5} \pm 2.92 \cdot 10^{-6}$	20.88
		2	$5.68 \cdot 10^{-3} \pm 0.19 \cdot 10^{-3}$	$3.39 \cdot 10^{-5} \pm 1.92 \cdot 10^{-6}$	13.67
		3	$6.06 \cdot 10^{-3} \pm 0.26 \cdot 10^{-3}$	$3.32 \cdot 10^{-5} \pm 2.90 \cdot 10^{-6}$	12.10
50	30	1	$5.92 \cdot 10^{-3} \pm 0.19 \cdot 10^{-3}$	$3.70 \cdot 10^{-5} \pm 4.20 \cdot 10^{-6}$	5.44
		2	$5.90 \cdot 10^{-3} \pm 0.13 \cdot 10^{-3}$	$3.60 \cdot 10^{-5} \pm 2.80 \cdot 10^{-6}$	3.65
		3	$5.81 \cdot 10^{-3} \pm 0.11 \cdot 10^{-3}$	$2.87 \cdot 10^{-5} \pm 2.39 \cdot 10^{-6}$	3.23
60	21	1	$5.55 \cdot 10^{-3} \pm 0.25 \cdot 10^{-3}$	$7.35 \cdot 10^{-5} \pm 6.00 \cdot 10^{-6}$	13.66
		2	$5.63 \cdot 10^{-3} \pm 0.28 \cdot 10^{-3}$	$8.35 \cdot 10^{-5} \pm 7.70 \cdot 10^{-6}$	16.16
		3	$5.70 \cdot 10^{-3} \pm 0.20 \cdot 10^{-3}$	$6.16 \cdot 10^{-5} \pm 3.85 \cdot 10^{-6}$	9.73
60	30	1	$5.91 \cdot 10^{-3} \pm 0.08 \cdot 10^{-3}$	$7.20 \cdot 10^{-5} \pm 2.32 \cdot 10^{-6}$	2.52
		2	$6.09 \cdot 10^{-3} \pm 0.09 \cdot 10^{-3}$	$8.26 \cdot 10^{-5} \pm 2.86 \cdot 10^{-6}$	2.95
		3	$6.08 \cdot 10^{-3} \pm 0.20 \cdot 10^{-3}$	$5.68 \cdot 10^{-5} \pm 5.24 \cdot 10^{-6}$	6.13
70	10	1	$6.04 \cdot 10^{-3} \pm 0.07 \cdot 10^{-3}$	$6.17 \cdot 10^{-5} \pm 1.88 \cdot 10^{-6}$	2.43
		2	$6.10 \cdot 10^{-3} \pm 0.05 \cdot 10^{-3}$	$5.65 \cdot 10^{-5} \pm 1.28 \cdot 10^{-6}$	1.72
		3	$6.07 \cdot 10^{-3} \pm 0.22 \cdot 10^{-3}$	$7.09 \cdot 10^{-5} \pm 6.06 \cdot 10^{-6}$	7.31
70	21	1	$6.13 \cdot 10^{-3} \pm 0.16 \cdot 10^{-3}$	$1.22 \cdot 10^{-4} \pm 6.87 \cdot 10^{-6}$	5.15
		2	$6.00 \cdot 10^{-3} \pm 0.10 \cdot 10^{-3}$	$1.15 \cdot 10^{-4} \pm 4.15 \cdot 10^{-6}$	3.22
		3	$6.01 \cdot 10^{-3} \pm 0.22 \cdot 10^{-3}$	$9.93 \cdot 10^{-5} \pm 8.35 \cdot 10^{-6}$	6.92
		4	$5.93 \cdot 10^{-3} \pm 0.24 \cdot 10^{-3}$	$1.76 \cdot 10^{-4} \pm 1.44 \cdot 10^{-5}$	8.85
		5	$6.05 \cdot 10^{-3} \pm 0.27 \cdot 10^{-3}$	$8.39 \cdot 10^{-5} \pm 8.30 \cdot 10^{-6}$	9.12
		6	$5.85 \cdot 10^{-3} \pm 0.18 \cdot 10^{-3}$	$1.36 \cdot 10^{-4} \pm 8.52 \cdot 10^{-6}$	7.15
		7	$5.98 \cdot 10^{-3} \pm 0.15 \cdot 10^{-3}$	$1.68 \cdot 10^{-4} \pm 8.62 \cdot 10^{-6}$	6.38
		8	$6.10 \cdot 10^{-3} \pm 0.17 \cdot 10^{-3}$	$2.23 \cdot 10^{-4} \pm 1.21 \cdot 10^{-5}$	7.56
		9	$6.53 \cdot 10^{-3} \pm 0.12 \cdot 10^{-3}$	$3.33 \cdot 10^{-4} \pm 1.18 \cdot 10^{-5}$	4.17
70	30	1	$5.72 \cdot 10^{-3} \pm 0.07 \cdot 10^{-3}$	$2.03 \cdot 10^{-4} \pm 5.10 \cdot 10^{-6}$	2.44
		2	$6.13 \cdot 10^{-3} \pm 0.29 \cdot 10^{-3}$	$2.70 \cdot 10^{-4} \pm 2.34 \cdot 10^{-5}$	11.48
		3	$5.94 \cdot 10^{-3} \pm 0.14 \cdot 10^{-3}$	$2.94 \cdot 10^{-4} \pm 1.29 \cdot 10^{-5}$	6.05
80	10	1	$6.28 \cdot 10^{-3} \pm 0.18 \cdot 10^{-3}$	$9.51 \cdot 10^{-5} \pm 5.96 \cdot 10^{-6}$	6.11
		2	$6.22 \cdot 10^{-3} \pm 0.18 \cdot 10^{-3}$	$9.12 \cdot 10^{-5} \pm 6.31 \cdot 10^{-6}$	5.40
		3	$6.50 \cdot 10^{-3} \pm 0.19 \cdot 10^{-3}$	$9.68 \cdot 10^{-5} \pm 6.50 \cdot 10^{-6}$	5.41
80	21	1	$6.11 \cdot 10^{-3} \pm 0.30 \cdot 10^{-3}$	$1.37 \cdot 10^{-4} \pm 1.46 \cdot 10^{-5}$	9.08
		2	$6.06 \cdot 10^{-3} \pm 0.26 \cdot 10^{-3}$	$1.32 \cdot 10^{-4} \pm 1.23 \cdot 10^{-5}$	8.17
80	30	1	$5.98 \cdot 10^{-3} \pm 0.17 \cdot 10^{-3}$	$2.94 \cdot 10^{-4} \pm 1.61 \cdot 10^{-5}$	4.87
		2	$6.08 \cdot 10^{-3} \pm 0.41 \cdot 10^{-3}$	$3.00 \cdot 10^{-4} \pm 3.81 \cdot 10^{-5}$	11.44
85	10	1	$6.37 \cdot 10^{-3} \pm 0.23 \cdot 10^{-3}$	$8.46 \cdot 10^{-5} \pm 5.79 \cdot 10^{-6}$	8.86
		2	$6.17 \cdot 10^{-3} \pm 0.24 \cdot 10^{-3}$	$1.14 \cdot 10^{-4} \pm 8.32 \cdot 10^{-6}$	8.64
		3	$6.97 \cdot 10^{-3} \pm 0.40 \cdot 10^{-3}$	$7.72 \cdot 10^{-5} \pm 8.59 \cdot 10^{-6}$	13.60
85	21	1	$6.18 \cdot 10^{-3} \pm 0.20 \cdot 10^{-3}$	$1.42 \cdot 10^{-4} \pm 7.99 \cdot 10^{-6}$	7.65
		2	$6.02 \cdot 10^{-3} \pm 0.22 \cdot 10^{-3}$	$1.83 \cdot 10^{-4} \pm 1.14 \cdot 10^{-5}$	9.73
		3	$6.16 \cdot 10^{-3} \pm 0.44 \cdot 10^{-3}$	$1.65 \cdot 10^{-4} \pm 2.03 \cdot 10^{-5}$	18.32
85	30	1	$5.82 \cdot 10^{-3} \pm 0.15 \cdot 10^{-3}$	$5.97 \cdot 10^{-4} \pm 3.44 \cdot 10^{-5}$	6.49
		2	$5.66 \cdot 10^{-3} \pm 0.16 \cdot 10^{-3}$	$4.36 \cdot 10^{-4} \pm 2.40 \cdot 10^{-5}$	5.89
		3	$5.76 \cdot 10^{-3} \pm 0.20 \cdot 10^{-3}$	$4.10 \cdot 10^{-4} \pm 2.84 \cdot 10^{-5}$	7.29
90	21	1	$6.13 \cdot 10^{-3} \pm 0.26 \cdot 10^{-3}$	$1.23 \cdot 10^{-4} \pm 1.08 \cdot 10^{-5}$	7.73
		2	$5.87 \cdot 10^{-3} \pm 0.31 \cdot 10^{-3}$	$1.76 \cdot 10^{-4} \pm 1.83 \cdot 10^{-5}$	9.05
		3	$5.88 \cdot 10^{-3} \pm 0.28 \cdot 10^{-3}$	$1.40 \cdot 10^{-4} \pm 1.41 \cdot 10^{-5}$	7.56
90	30	1	$6.33 \cdot 10^{-3} \pm 0.41 \cdot 10^{-3}$	$3.01 \cdot 10^{-4} \pm 3.49 \cdot 10^{-5}$	13.43
		2	$6.00 \cdot 10^{-3} \pm 0.43 \cdot 10^{-3}$	$3.27 \cdot 10^{-4} \pm 4.26 \cdot 10^{-5}$	15.60
		3	$5.72 \cdot 10^{-3} \pm 0.34 \cdot 10^{-3}$	$3.07 \cdot 10^{-4} \pm 3.24 \cdot 10^{-5}$	12.35