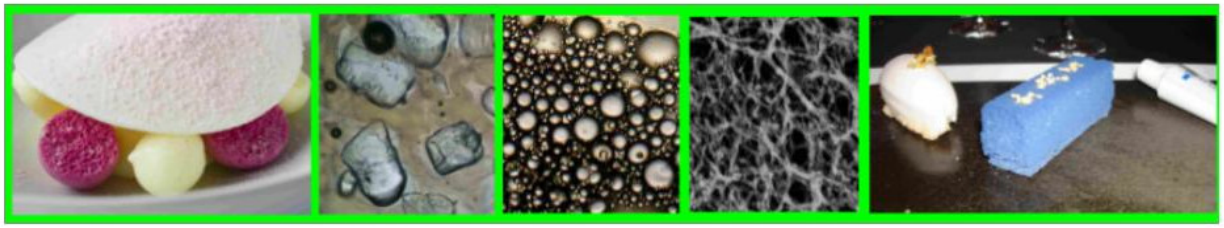

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Authors
Laetitia Le Falher, Vincent Faugeras, Delphine Lioger, Francisco X. Deolarte, Hervé This

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Time-Course Evolution of Two Water-soluble Vitamins (Ascorbic acid, Nicotinic acid) and Two Amino-Acids (L-Cysteine and L-Methionine) Following Thermal Processing in Water at 100 °C (part II)

Laetitia Le Falher,[a,b*] Vincent Faugeras,[a,b] Delphine Lioger,[a] Francisco X. Deolarte,[c] Hervé This[b, d]

[a] *Innit SAS, 76 rue de la pompe, F-75116 Paris, France.*
[b] *Groupe de Gastronomie Moléculaire, AgroParisTech-Inra, Laboratoire de Chimie Analytique, F-75005 Paris, France.*
[c] *Innit Inc, 600 Allerton – Suite 101 - Redwood city, California, United States.*
[d] *UMR Ingénierie Procédés Aliments, AgroParisTech, Inra, Université Paris-Saclay, 91300 Massy, France*

Discussion:

For ascorbic acid, the data points were first arbitrarily fitted by a negative exponential curve in order to investigate the first-order reaction. R^2 was found to be equal to 0.9992, which, taking into account uncertainties, could be coherent with a first-order reaction (Figure 2, (A)).

Data were analyzed by a one-way ANOVA ($p < 0.01$). Each time group was then compared with the previous time group using the Student *t* test.

A significant difference was found between means of masses at different times ($p < 0.05$) (Table 1). This profile of degradation may be explained by a low content in oxygen in water at 100 °C [14]. Indeed, ascorbic acid does not oxidize in its unstable form, dehydroascorbic acid, and thus the

kinetics of degradation in anaerobic conditions is slower than in aerobic conditions [10,15,16]. The observation of traces of furfural confirms that the conditions used are anaerobic [15,17].

The amount of L-cysteine decreased following a linear trend. The points were first fitted by a zero order reaction. R^2 was found

Table 1. Time-course degradation of compounds of interest. a: Significantly different from T1 (Student t *Test,* p *< 0.01). b : Significantly different from T2 (Student* t *Test,* p *< 0.05). c : Significantly different from T3 (Student* t *Test,* p *< 0.01). d : Significantly different from T4 (Student* t *Test,* p *< 0.01). e : Significantly different from T5 (Student* t *Test,* p *< 0.01). NS: Not Significant by a one-way ANOVA (*p *> 0.05). For the calculations of percentage, we considered that there is no degradation at 0.17 hour of reaction given the slow degradation of nutrients.*

to be equal to 0.9945 which, taking into account uncertainties, could be coherent with a zero-order reaction (Figure 2, (C)). Data were analyzed by a one way ANOVA ($p < 0.01$). Each time group was then compared with the previous time group using the Student t test. A significant difference was found between the means of masses from 48 h ($p < 0.01$) (Table 1).

For nicotinic acid and L-methionine, the apparent absence of degradation was checked by a one-way ANOVA of data. It was calculated that there is no significant difference between means of masses at different time ($p > 0.05$) (Table 1). These results are in accordance with previous studies since nicotinic acid is reported to be a stable vitamin to temperature, dioxygen and oxidizing conditions [5]. Nevertheless, to our best knowledge, the reactivity of pure L-methionine is not described in aqueous media.

In order to understand the stability of L-nicotinic

acid and L-methionine, we take into account the fact that any chemical reaction is the result of breaking and making of chemical bonds. For such

Compound	Time (h)	Mass of compound (SD) (g)	Mass percentage (%) (SD)
ascorbic acid	0.17	T1 = 0.0125 (0.0005)	100
	15	T2 = 0.0096 (0.0005) [a]	77 (5)
	24	T3 = 0.0083 (0.0004) [b]	66 (5)
	48	T4 = 0.0051 (0.0002) [c]	41 (4)
	72	T5 = 0.0033 (0.0001) [d]	26 (2)
	96	T6 = 0.0022 (0.0002) [e]	18 (10)
nicotinic acid	0.17	T1 = 0.0100 (0.0005) [NS]	100
	24	T2 = 0.0100 (0.0005) [NS]	100 (5)
	48	T3 = 0.0103 (0.0002) [NS]	103 (2)
	72	T4 = 0.0100 (0.0003) [NS]	100 (3)
	96	T5 = 0.0099 (0.0003) [NS]	99 (4)
L-cysteine	0.17	T1 = 0.0096 (0.0006)	100
	24	T2 = 0.0083 (0.0008)	86 (9)
	48	T3 = 0.0070 (0.0004) [a]	73 (5)
	72	T4 = 0.0054 (0.0002) [c]	56 (5)
	96	T5 = 0.0036 (0.0005) [d]	38 (14)
L-methionine	0.17	T1 = 0.0101 (0.0006) [NS]	100
	24	T2 = 0.0100 (0.0009) [NS]	99 (9)
	48	T3 = 0.0105 (0.0009) [NS]	104 (9)
	72	T4 = 0.0109 (0.0002) [NS]	108 (2)
	96	T5 = 0.0107 (0.0008) [NS]	106 (7)

phenomena the thermal energy of the medium is important. Of course, depending on the particular reaction environment, two extreme possibilities can be considered: homolytic or heterolytic reactions. In both cases, the thermal energy k_B T of the reaction mixture (k_B being the Boltzmann constant, and T the absolute temperature) can be compared with the bond enthalpy of compounds being thermally processed. If the energy given by water molecules is greater than the energy of a chemical bond, the latter is broken.

For homolytic bonds, the energy required for cleavage at 298 K corresponds to the enthalpy of the reaction AB → A + B, which is by definition the bond dissociation enthalpy of the molecule AB. At 100 °C, the thermal energy $k_B T$ is of the order of 3.1 kJ/mol. The order of magnitude of energy of chemical bonds in our compounds of interest is of 400 kJ/mol which is 100 times bigger than the thermal energy [18]. This shows that the probability of breaking of the chemical bonds of the molecules of interest is low (this means that the reaction rate is about 10^{43} slower than the reaction rate for a thermal energy equal to the bond enthalpy, assuming an Arrhenius law).

For heterolytic bond cleavage, the energies are generally lower than for homolytic cases.

For ascorbic acid, the energy needed for breaking bond was not experimentally measured according to the literature, but the degradation of compounds similar to ascorbic acid, lactones, was studied [19].

For such compounds, in which the ring-strained nature is a factor of destabilization (low bond energy), degradation occurs particularly through hydrolysis. Kaiser and Kézdy have shown that small structural variations in the molecules can have large effects on their reactivity, especially in β-lactones [20]. They used polarizable continuum model (PCM) calculations which take into account the contribution of solvation free energy to the total energy, and thus afford ΔG with appropriate statistical thermodynamics and solvation terms. Using this model, enthalpy values include the statistical thermodynamics enthalpic term plus the solvation free energy contribution.

They found that for β-isovalerolactone, which is the closest lactone to ascorbic acid, the energy barriers calculated for the most favorable mechanism (base catalyzed alkyl-oxygen cleavage) is 79.7 kJ/mol, whereas the experimental value is 87 kJ/mol [21]. This is more than 20 times the thermal energy.

Finally, a comparison of the thermal energy and the bond energy shows that all our compounds of interest have reasons to be stable in our experimental conditions. When instability is observed, medium effects have to be considered. In particular, solubility in water has to be taken into account for interpreting the possible destabilization of the activated complex formed from the compounds of interest and water molecules; it is well-known that such energy barrier (or intermediate state) determines both the kinetic and the thermodynamics of chemical modifications [22].

Conclusion

Quantification by isq ^{1}H NMR method allowed us to determine the half-life of isolated ascorbic acid (38 h) and L-cysteine (80 h) in water at 100 °C. No significant change of behavior of nicotinic acid or L-methionine was observed. Identification of degradation products of

ascorbic acid and L-cysteine should also be carried out by ^{1}H NMR. These experiments show that more work has to be done in order to explore phenomena occurring in this simple system of aqueous solutions. *Is*q NMR is a suitable tool for studying the behavior of the starting material but more precise analytical methods are needed in order to determine the reaction products, and the possible reaction mechanisms.

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