Kinetic and thermodynamic study of the photochemical degradation of patulin

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ABSTRACT

In a previous work, the UV photodegradation of patulin was concluded to follow a first-order kinetic and to be faster at acidic pH. In this case, the UV photodegradation of aqueous patulin solutions was studied at acidic pH values (3–6) similar to the values of apple juices where patulin has been found, obtaining that the first-order kinetic constant increased when the acidity of the reaction media was also increased (pH decreased). From the parameters obtained by fitting the experimental data to both the Arrhenius and Van't Hoff equations, the existence of kinetic and thermodynamic compensations was studied. Apparent kinetic and thermodynamic compensations were concluded, the isokinetic and isoequilibrium temperatures being −13.4 and −15.4 °C, respectively. As the harmonic mean temperature was 34.3 °C, applying the statistical criterion, it was concluded that both compensations were real, the reaction mechanism control changing from enthalpic for temperatures lower than the isokinetic-isoequilibrium temperatures (−13.4/−15.4 °C) to entropic for higher temperatures. It could also be concluded that the reaction rate depends on the pH value for the acidic range studied.

1. Introduction

Patulin (PAT) is a mycotoxin produced by fungi that has been found in apple juices and nectars (Marín et al., 2011). As PAT was shown to be mutagenic and to cause neurotoxin, immunotoxic, genotoxic and gastrointestinal effects in rodents (Hopkins, 1993), the maximum tolerance limit in juices was established at 10–50 μg/kg (European Commission, 2003; FDA-U.S. Food and Drug Administration, 2004; WHO, 1995). PAT has to be minimized by removing and trimming decayed and damaged fruit but fungal growth can occur internally (Bosco & Mollea, 2012) and the contamination can also appear or be increased during storage. So, as PAT is resistant to the usual thermal treatments (Acar, Gokmen, & Taydas, 1998; Wheeler, Harrison, & Koehler, 1987), alternative methods to treat apple-based products are required once the juice has been contaminated.

The main alternative methods studied are filtration (Huebner et al., 2000), adsorption (Kadakal & Nas, 2002), ozone (McKenzie et al., 1997), pressure (Bruna, Voldrich, Marek, & Kamarad, 1999), ionizing irradiation (Zegota, Zegota, & Bachmann, 1988), pulsed light (Funes, Gómez, Resnik, & Alzamora, 2013) and addition of chemical additives such as sulphur compounds (Burroughs, 1977), ascorbic acid (Brackett & Marth, 1979), thiamine hydrochloride, pyridoxine hydrochloride and calcium pantothenate (Yazici & Velioglu, 2002), sodium benzoate (Roland, Beuchat, Worthington, & Hitchcock, 1984),

potassium sorbate and sodium propionate (Lennox & McElroy, 1984). Most of these alternative methods provoke great changes to the final juice or are unable to eliminate the total PAT content.

UV irradiation of PAT was previously studied (Assatarakul, Churey, Manns, & Worobo, 2012; Tikekar, Anantheswaran, & LaBorde, 2014; Zhu, Koutchma, Warriner, Shao, & Zhou, 2012; Zhu, Koutchma, Warriner, & Zhou, 2014) but exclusively at the germicidal wavelength of 254 nm or within the UVC range.

The effect of the UV irradiation on fruit juices was studied for apple (Falguera, Pagán, & Ibarz, 2011), grape must (Falguera, Garza, Pagán, Garvín, & Ibarz, 2013) and pear (Falguera, Garvín, Garza, Pagán, & Ibarz, 2014) and in all cases the application of UV irradiation almost totally inactivated Polyphenol oxidase (PPO), Peroxidase (POD) and Pectinmethylesterase (PME) enzymes, as it was desired in order to avoid changes. However, no variations were observed in pH, soluble solid content, formol index, total phenolics and sugars. The colour changed slightly due to the probably impairment of some pigments present in the juice. The only undesirable change was the loos of vitamin C content, showing decreases from 4 to 70% after two-hour irradiation.

In the previous study of Ibarz et al. (2014), PAT was concluded to absorb radiation between 200 and 350 nm and its degradation was confirmed by UV–Vis irradiation (255–755 nm). The concentration of patulin to be irradiated was chosen to be 500 μg/kg, a value clearly

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higher than the legal limit of between 10 and 50 μg/kg, in order to know if a contaminated juice could be driven below the limit established by the rules. The reaction was concluded to follow first-order kinetics and showed a faster reaction rate for acidic pH (pH = 4) than for neutral value (pH = 7). The first-order kinetic constants also showed that the higher the temperature, the higher the value, although the values were not fitted to the Arrhenius equation. This study also calculated the absorbed radiation by PAT and also showed its degradation in apple juice, obtaining a lower rate than in the case of aqueous solutions, probably due to the fact that some juice components absorb radiation causing a photoprotection effect. In this same previous study of Ibarz et al. (2014), a three-stage reaction mechanism was proposed (through an excited PAT molecule that could decline to its previous state or change to the photoproduct) and the absorbed radiation was concluded to depend linearly on the patulin concentration for levels below 500 μg/kg, as expected when the concentration of the absorbant is low enough (Garvín, Ibarz, & Ibarz, 2015). Both considerations were used to conclude a first-order kinetic model (Eq. (1)) that matched the experimental data giving very good fits and obtaining the corresponding kinetic constants at pH 4 and 7.

$$C_P = C_P^0 \exp(-kt) \tag{1}$$

C_P being the concentration of PAT, $C_P{}^0$ the initial concentration of PAT, t the irradiation time and k the kinetic constant.

Kinetic and thermodynamic compensations have been reported in many chemical, physical, biological and food processes (Liu & Guo, 2001). Kinetic compensation only takes place when the logarithm of the frequency factor ($\ln k_0$) happens to depend linearly on the activation energy (E_a) (Garvín, Ibarz, & Ibarz, 2017) (Eq. (2)), both parameters being the fittings of the linearized Arrhenius equation (Eq. (3)) for different values of an environmental variable (pH in this case).

$$\ln k_0 = a + bEa \tag{2}$$

$$\ln k = \ln k_0 - \frac{E_a}{R}\frac{1}{T} \tag{3}$$

The isokinetic temperature (T_{isokin}) is a mathematical consequence exclusively for this situation and is the temperature at which the kinetic constant is approximately the same for each pH value. Comparing Eqs. (2) and (3), the T_{isokin} can be obtained from the fitted parameters of Eq. (2):

$$T_{isokin} = \frac{1}{bR} \tag{4}$$

and the kinetic constant at the T_{isokin} can be obtained as:

$$\ln k(T_{isokin}) = a \tag{5}$$

The thermodynamic compensation can similarly be found for equilibrium situations, from the Van't Hoff equation (Eq. (6)) when the enthalpy variation (ΔH) happens to depend linearly on the entropy variation (ΔS) (Eq. (7)) (Garvín et al., 2017).

$$\ln K_{eq} = \frac{\Delta S}{R} - \frac{\Delta H}{R}\frac{1}{T} \tag{6}$$

$$\Delta H = A + B\Delta S \tag{7}$$

From the equilibrium constant (K_{eq}), the Gibbs free energy (ΔG) can also be obtained:

$$\Delta G = -RT \ln K_{eq} \tag{8}$$

For these equilibrium situations, the isoequilibrium temperature (T_{isoeq}) is also a mathematical consequence and corresponds to the temperature at which the equilibrium constant is approximately the same for each pH value. Comparing Eqs. (6) and (7), the T_{isoeq} can be obtained from the fitted parameters of Eq. (6):

$$T_{isoeq} = B \tag{9}$$

and the equilibrium constant and the Gibbs free energy both at the T_{isoeq} can be obtained as:

$$\ln K_{eq}(T_{isoeq}) = -\frac{A}{RT_{isoeq}} \tag{10}$$

$$\Delta G(T_{isoeq}) = A \tag{11}$$

For chemical reactions, the transition state theory can be applied and thus the kinetic constant of the global reaction (k) can be related to the equilibrium constant between the reagent and the transition state (K_{eq}) (Eyring & Wynne-Jones, 1935).

$$k = \frac{k_B T}{h} K_{eq} \tag{12}$$

k_B being the Boltzmann's constant ($1.381 \cdot 10^{-23}$ J·K^{-1}) and h the Plank constant ($6.626 \cdot 10^{-34}$ J·s). For these cases, the thermodynamic parameters (enthalpy, entropy and Gibbs free energy) refer to this specific equilibrium stage between the reagents and the transition state (activation complex) and are called activation enthalpy ($\Delta H^{\neq}$), activation entropy ($\Delta S^{\neq}$) and activation Gibbs free energy ($\Delta G^{\neq}$).

Thus, only when the transition state theory can be applied, if one kind of compensation happens to take place, it can be concluded (Garvín et al., 2017) that the other also has to occur and both the isokinetic and the isoequilibrium temperatures have to be approximately the same (e.g., Aguilar, Garvín, Azuara, & Ibarz, 2016; Ibarz, Garvín, Rojas, Azuara, & Ibarz, 2016).

Krug, Hunter, and Grieger (1976a) demonstrated that the propagation of experimental errors tends to distribute the estimates of the kinetic compensation ($\ln k_0$ and E_a, both obtained from ordinary linear regression of the Arrhenius equation) following a linear relation that is called statistical compensation. Comparing the slope of the statistical compensation, it was concluded that if the experimental harmonic mean temperature (T_{hm}) was outside the confidence interval for the isokinetic temperature, a real compensation could be concluded and the effect of the environmental variable (pH) would be confirmed. However, if T_{hm} fell within the confidence interval for the isokinetic temperature, it would have to be concluded that the linear relationship between $\ln k_0$ and E_a was the consequence of the propagation of experimental errors, the apparent observed compensation being actually statistical compensation.

$$T_{hm} = \frac{n}{\sum_{i=1}^{n} \frac{1}{T_i}} \tag{13}$$

Due to the similarity between the Arrhenius and Van't Hoff equations, exactly the same occurs for thermodynamic compensation.

In order to distinguish between real and statistical compensation, Krug, Hunter, and Grieger (1976b) proposed a method that makes estimates independent of one another, consisting of centering the independent variable defined as inverse experimental temperature about its mean ($1/T_{hm}$).

Many authors have concluded that both kinds of compensation are unreal and arise from the uncertainties and errors in the measurements of the kinetic or equilibrium parameters along with the statistical problems associated with the linear regression of parameters previously also fitted by linear regression that are mutually interdependent (Petersen, Markgraf, & Ross, 1961; Exner, 1964; Sharp, 2001; Starikov & Norden, 2007; Barrie, 2012a, 2012b; Starikov, 2013; Perez-Benito, 2013). They all seem to be right, but this argument is included in the criterion defined by Krug et al. (1976a) to distinguish real compensation from statistical one. Some other authors have stated that both kinetic and thermodynamic compensation are artefacts or a phantom phenomenona (e.g., McBane, 1998; Cornish-Bowden, 2002; Perez-Benito, 2013), but none of them have been able to demonstrate that it is always an artefact or a phantom phenomenon, nor found the reason why the linear relationship related to any kind of compensation