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Kinetics of the glucose/glycine Maillard reaction pathways: influences of pH and reactant initial concentrations

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Abstract

A previously proposed kinetic model for the glucose/glycine Maillard reaction pathways has been validated by changing the initial pH (4.8, 5.5, 6.0, 6.8 and 7.5) of the reaction and reactant initial concentrations (1:2 and 2:1 molar ratios were compared to the 1:1 ratio). The model consists of 10 steps, each characterised by a rate constant. The initial pH had a different effect on the various rate constants, and the results suggest a mixture between specific acid and base catalysis. pH–rate profiles were established and, from these, a quantitative relationship was derived: $k_{obs} = k_e(10^{pD \times pH})$, in which k_{obs} is the estimated rate constants from experiments, k_e an expression for the elementary reaction, and pD the parameter describing the pH-dependence. The parameters k_e and pD were estimated from the pH–rate profiles. This equation thus expresses the pH-dependence of rate constants in much the same way as the Arrhenius equation does for the temperature-dependence of rate constants. The initial concentrations of glucose and glycine did not have an effect on the estimated rate constants, indicating that the model is robust to change in initial concentrations of the reactants. Finally, a sensitivity analysis of the model was performed to highlight the important steps, as well as finding possible redundant ones. Again, the model performed well; all steps were important and the model was consistent with the established reaction mechanism.

Keywords: Kinetics; Maillard reaction; pH–rate profile; Multiresponse modelling; Glucose; Glycine

1. Introduction

From a technological point of view, controlling food quality means controlling chemical, physical and microbiological changes during food processing and storage. However, to be able to do that, the reactions of interest need to be studied in a quantitative way. Kinetic parameters describing such changes are thus needed.

The Maillard reaction, also known as the reaction between carbonyls and amines or non-enzymatic browning, strongly affects food quality. Not only does it influence food sensorial properties, such as flavour and colour, but also nutritional and health aspects (Finot, Aeschbacher, Hurrell, & Liardon, 1990; Horiuchi, Taniguchi, Hayase, Kurata, & Osawa, 2002; Labuza, Reineccius, Monnier, O'Brien, & Baynes, 1994; Waller & Feather, 1983). Knowledge of the kinetic parameters, such as reaction order, rate constant and activation energy, is essential for predicting and controlling food quality attributes associated with the Maillard reaction. In previous studies, multiresponse kinetic modelling (i.e., taking more than one reactant and product into consideration in the modelling process) proved to be a powerful tool to model complicated consecutive and parallel reactions as occur in the Maillard reaction (Brands & Van Boekel, 2002; Brands & Van Boekel,

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2003; Martins & Van Boekel, 2003a; Martins & Van Boekel, 2004). Such a multiresponse approach provided major guidance for understanding the reaction mechanism. The main advantages of this approach are that models can be tested more rigorously and, once the goodness of fit is deemed acceptable, estimation of the parameters can be done much more precisely than with the common uniresponse approach.

Kinetic model validation is often achieved by changing important reaction conditions to investigate how robust the model is and how consistent it is with the established reaction mechanism (Van Boekel, 1996, 2001). The course of the Maillard reaction can be affected by many factors, such as buffer, pH, temperature, reactant concentrations and the ratio between reactants. A buffer may exert a specific effect as catalyst of the reaction (Bell, 1997; Rizzi, 2004). With regard to the influence of pH on the Maillard reaction, Labuza and Baisier (1992) observed that the substrate loss increased with increasing pH, up to a pH of about 10, with little if any browning occurring below pH 6. Nicoli, Anese, and Lerici (1993) observed a smooth increase in browning and rate constants with pH between 2 and 8, but a rather abrupt increase between pH 8 and 10. The latter phenomenon is also obvious from work published by Ajandouz and Puigserver (1999) and Ajandouz, Tchiapke, Dalle Ore, and Puigserver (2001). Furthermore, the main degradation pathways of the Amadori compound, namely enolisation and retro-aldolisation, were shown to be strongly dependent on the reaction pH (Huyghues-Despoints & Yaylayan, 1996; Ledl & Schleicher, 1990; Smith & Thornalley, 1992). The pH-dependence of the Maillard reaction for the amino acid reagent can, at least qualitatively, be described by the effect of protonation of the amino acid. The amount of unprotonated amino group, which is considered to be the reactive species, increases obviously with increasing pH. Furthermore, pH has an effect on the reactant sugar. First, the open chain form of the sugar is considered to be the reactive species, and the amount of open chain increases with pH (Yayalayan, Ismail, & Mandeville, 1993). Second, the formation of the enediol anion is considered a key reaction in both reversible and irreversible sugar reactions (De Bruin, 1986). Reversible sugar reactions are ionisation, mutarotation, enolisation and isomerisation, and these reactions imply that the sugar moiety remains intact. Irreversible sugar reactions imply that the sugar moiety is degraded in, eventually, organic acids. Since ionisation is a rate-determining step (De Bruin, 1986), pH obviously has an influence on sugar reactions and hence on the Maillard reaction. All in all, the initial step of the Maillard reaction is highly influenced by the initial pH of the reaction. However, since the Maillard reaction consists of several reaction steps, some of which are acid–base catalysed, pH may have a considerable effect on which reaction route prevails and which products are formed. In all kinetic models published so far, including ours, pseudo rate constants, or observed rate constants, are used, which actually include pH-dependent rate constants, and do not include, for instance, sugar anions and the key intermediates, enediol anions, since these concentrations are assumed to be proportional to the total sugar concentrations (De Bruin, 1986). Since the pseudo rate constants do include pH-dependence, study of so-called pH–rate profiles can be helpful as a starting point for development of mechanistic hypotheses (Loudon, 1991). This author considered five possible options:

1. The observed rate constant is independent of pH: $k_{\text{obs}} = c_1$.
2. The observed rate constant is directly proportional to H^+ ions: $k_{\text{obs}} = c_2[\text{H}^+]$.
3. The observed rate constant is inversely proportional to H^+ ions (or equivalently directly proportional to $[\text{OH}^-]$): $k_{\text{obs}} = c_3/[\text{H}^+]$.
4. The observed rate constant is independent of pH at low pH and directly proportional to pH at high pH: $k_{\text{obs}} = c_4[\text{H}^+]/(c_5+[\text{H}^+])$.
5. The observed rate constant is inversely proportional to pH at low pH and independent at high pH: $k_{\text{obs}} = c_6/(\text{c}_7 + [\text{H}^+])$.

Besides pH, initial concentrations and ratio of the reactants should also have a significant impact on the reaction. Kato, Yamamoto, and Fujimaki (1969) observed that, at low concentrations of glycine, fructose browned faster than glucose, whereas, at high amino acid concentration, the reverse occurred. However, it should be noted that the *rate* of browning and the *rate constant* of the step in the reaction network that results in colour formation, are two different things. In fact, increasing the initial reactant concentrations should *not* influence the reaction rate constants since, for the reaction of sugar (S) with the amino acid (A), it follows that:

$$-\frac{\mathrm{d}[S]}{\mathrm{d}t} = -\frac{\mathrm{d}[A]}{\mathrm{d}t} = k_1[S][A].$$

The overall rate of loss of the S and the A is equal to the rate constant times their concentration. Obviously, the overall *rate* does depend on concentration.

Maillard browning of course increases with temperature. However, each step within the Maillard reaction network may have different temperature sensitivity and, as a result, temperature may strongly determine which reaction route prevails. Recently, the influence of temperature on the glucose/glycine Maillard reaction was studied and a comprehensive kinetic model was proposed, which is reproduced here as Scheme 1 (Martins & Van Boekel, 2004). Using multiresponse kinetic analysis, the temperature-dependence of the various degradation