

Kinetics of Acrylamide Formation and Elimination during
Heating of an Asparagine–Sugar Model System

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The kinetics of acrylamide (AA) was analyzed by heating a simple model system consisting of asparagine and glucose, fructose, or sucrose (0.01 M, pH 6) at temperatures between 140 and 200 °C. The AA concentration appeared to be the net result of simultaneous formation and elimination. A general kinetic model describing the AA yield was identified, and kinetic parameters were obtained by nonlinear regression on the nonisothermally derived data. On the basis of kinetic parameters, the AA formation appeared to proceed faster and to be more temperature sensitive in the asparagine–glucose than in the asparagine–fructose model system. The AA elimination kinetics, on the other hand, was similar. Significantly less AA was formed in the asparagine–sucrose model system as compared to the model systems with glucose or fructose.

KEYWORDS: Acrylamide; kinetics; asparagine; glucose; fructose; sucrose

INTRODUCTION

Acrylamide (AA, CAS 79-06-1) is an industrial chemical used since the mid-1950s in the production of polyacrylamides for different technical applications (e.g., in the paper and textile industry, as soil conditioners, and in wastewater treatment). Recently, relatively high levels of AA have been measured in different food and food products (1–3). AA appeared to be formed during high temperature processes such as frying, baking, and roasting of foods, especially of carbohydrate-rich foods. The neurotoxicity of AA in humans is well-known from occupational and accidental exposures. In addition, experimental studies with AA in animals have shown reproductive, genotoxic, and carcinogenic properties (4–6).

Since the finding of AA in food, intensive research in several areas is ongoing and focuses mainly on the different mechanisms of AA formation, the toxicology of AA (e.g., bioavailability, intake evaluation, and margins of exposure), the development of accurate analytical techniques (e.g., the development of a uniform method applicable to all food matrices and of cheap and rapid screening methods), and the effect of the food composition on the AA yield (e.g., variation due to cultivar and storage temperature of potato tubers). Several strategies for reducing AA have been put forward and are under investigation (7, 8). To predict and to control the amount of AA formed, additionally, kinetics of AA as a function of process and product variables need to be known. Reported data are, however, mainly qualitative in nature, and until now, quantitative data on the possible interaction between time, temperature, and AA formation were lacking (9, 10).

In this paper, a kinetic model allowing the estimation of the AA yield in terms of processing time and temperature is identified. Several research groups previously identified the importance of the amino acid asparagine and the Maillard reaction in the formation cascade of AA. Other probably minor pathways have been proposed as well, including acrolein and acrylic acid (11–14). Because of the inherent complexity of a food matrix, where many factors are involved that act one upon another, we chose to analyze kinetics under idealized conditions in a closed asparagine–glucose model system. Whereas no or only trace amounts of AA have been reported in a model system consisting of glucose and an amino acid other than asparagine (11, 12, 15), a variety of monosaccharides (e.g., glucose, deoxyglucose, ribose, glyceraldehyde, and glyoxal) can generate AA from asparagine (14). Therefore, in addition to the asparagine–glucose model system, AA formation/elimination kinetics were also analyzed in asparagine–fructose and asparagine–sucrose model systems. Glucose, fructose, and sucrose are the most common sugars of the potato (constituting >90% of all sugars in a potato tuber), and potato products yield the highest AA amounts when fried or baked. Additionally, studying kinetics in those three model systems allows comparison between the performance of an aldohexose and a ketohexose sugar and the performance of a disaccharide and a monosaccharide.

MATERIALS AND METHODS

Model System and Heat Treatment. Model systems were prepared by dissolving 0.01 M L-asparagine (≥99.5%, Sigma-Aldrich, Bornem, Belgium) and 0.01 M D-glucose, D-fructose, or D-sucrose (≥99%, Sigma-Aldrich) in a 0.05 M citrate buffer with a pH of 6.

To eliminate as much side phenomena as possible during heating (such as fluctuations in water activity due to water evaporation and

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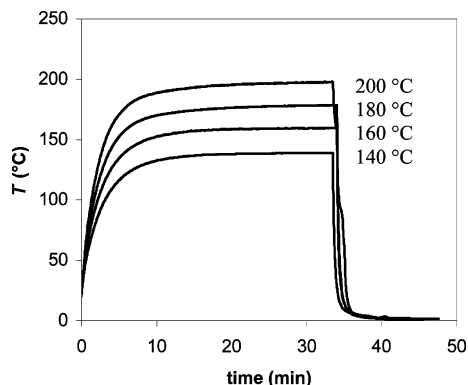


Figure 1. Typical temperature–time profiles of samples heated in closed reactors.

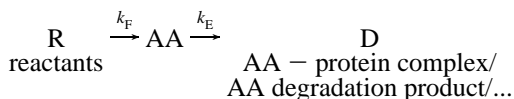
absorption of oil), which affect AA formation, samples were heated in hermetically closed reactor tubes (inox, 8 mm × 100 mm, custom-made). After the samples were heated in a thermostated oil bath at temperatures between 140 and 200 °C for different heating times, the samples were immediately cooled in ice water to stop any further reaction. Because the samples went through a heating phase, the temperature profile of each sample was registered in the reactor tubes in order to obtain an accurate analysis of formation and elimination kinetics of AA. An example of typical temperature profiles is given in **Figure 1**. Similar profiles were used in each assay, for which temperature–time data were measured at regular time intervals (2 s) using thermocouples (type T, Thermo Electric, Balen, Belgium) connected to a datalogger (TM 9616, Ellab, Norfolk, England).

Analysis of AA. The AA content was determined by a gas chromatography–mass spectrometry (GC-MS) method (without previous derivatization of AA), described by Biedermann et al. (16). After AA extraction and further cleanup of the sample, 1 μ L was injected cool-on-column on an HP-INNOWax column (30 m × 250 μ m i.d., 0.25 μ m ft, equipped with a 0.5 m × 530 μ m i.d. precolumn of deactivated fused silica, Agilent Technologies, Diegem, Belgium) coupled to a quadrupole mass spectrometer operating in positive chemical ionization with He as the carrier gas and CH₄ as the ionization gas (5973 inert GC-MS system, Agilent Technologies).

The AA concentration at (*m/z* 72) was quantified by adding an internal standard, methacrylamide (*m/z* 86), at the beginning of the sample preparation step. By comparing this internal standard with a second internal standard, i.e., butyramide (*m/z* 88), which was added to the samples before injection, we could account for losses during analysis.

DATA ANALYSIS

Kinetic Parameter Estimation. Simplified, the formation of AA in food can be given by the following scheme, with k_F and k_E the formation and elimination rate constants, respectively, at the temperature studied (7)



Because asparagine and sugar are present at an equimolar level in the model system, the formation of AA from these reactants can be modeled by a second-order reaction. Biedermann et al. (17), monitoring AA elimination by D₃-AA, proposed (pseudo-) first-order kinetics for describing the AA elimination. Consequently, the net AA content (C_{AA}) can be described by following equation:

$$\frac{dC_{AA}}{dt} = k_F(C_{asn} \cdot C_{sugar}) - k_E C_{AA} \quad (1)$$

with C_{asn} , C_{sugar} , and C_D the concentration of asparagine, sugar, and D, respectively, and t the treatment time. It is clear that, next to isotopically labeled AA, elimination of AA can also be deduced from the kinetic model fitted on the net formation data of AA.

Only a fraction of the asparagine and the sugar is converted into AA (10). Because the asparagine and the sugar are reacted at an equal concentration, the concentration of asparagine (C_{asn}) can be assumed to be equal to the concentration of the sugar (C_{sugar}) and equal to C_R :

$$\frac{dC_{AA}}{dt} = k_F(C_R)^2 - k_E C_{AA} \quad (2)$$

However, whereas both asparagine and sugar undergo the Maillard reaction, the sugar is consumed by caramelization reactions as well. Moreover, in the Maillard reaction, the loss of sugar has been reported to be faster than the loss of amino acid, which could be explained by the regeneration of asparagine from the initial condensation products and the possible formation of diglucosylamine (18). On the basis of these arguments, asparagine can be considered in excess as compared to the sugar. As a result, the AA yield can be described by a first-order formation/first-order elimination kinetic model and eq 2 becomes (7, 19)

$$\frac{dC_{AA}}{dt} = k_F C_R - k_E C_{AA} \quad (3)$$

Kinetic models are not mechanistic models; they describe the rates of formation of substances in terms of the rate-limiting processes.

When kinetics are analyzed under isothermal conditions (constant temperature), k values can be assumed constant and the above equations are easily integrated. However, because heating of the samples involved nonisothermal conditions (variable temperature), the integrated effect of temperature on the reaction rate constant has to be taken into account.

Generally, the effect of temperature on the reaction rate constant k can be expressed by the Arrhenius relation (20), in which the temperature dependence of k is quantified by the activation energy E_a (J/mol) according to

$$k = k_{ref} \exp \left[\frac{E_a}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (4)$$

with R the universal gas constant (8.314 J/mol, K), T the temperature concerned (K), and k_{ref} the reaction rate constant at reference temperature T_{ref} . This equation applies for each rate constant involved in the kinetic model describing AA formation/elimination.

After implementation of eq 4 in eqs 2 or 3, the resulting differential equations were solved by numerical integration (Euler) of the registered temperature–time profile of each sample, and kinetic parameters describing AA formation and elimination (k_{Fref} , E_{aF} , and k_{Eref} , E_{aE} , respectively) could be estimated by nonlinear regression (Gauss–Newton algorithm). Data analysis was performed by the statistical software package SAS (v8, Cary, NC).

Evaluation of the Kinetic Model. The performance of the model was evaluated in terms of output statistics that evaluate the quality of fitting and parameter estimation, i.e., the sum of squares (SS) and the standard errors (SE) associated with the parameter estimates. Commonly, the R^2 value is used to express the quality of fit of a linear model. Use of the R^2 for evaluating

Table 1. Relative AA Content (%) in Equimolar Asparagine–Sugar Model Systems (0.01 M, pH 6) Heated at Different Temperatures

T (°C)	glucose	fructose	sucrose
140	100	100.0 ± 11.1 ^a	45.8 ± 12.2
160	100	78.4 ± 28.8	40.8 ± 16.9
180	100	63.5 ± 5.0	41.6 ± 18.5
200	100	54.7 ± 2.5	51.0 ± 20.4

^a Averages ± standard deviations of nine samples taken after different treatment times at the temperature concerned.

nonlinear models, however, can be highly misleading. One of the problems with the R^2 definition is that it requires the presence of an intercept, which most nonlinear models do not have. Therefore, a coefficient of determination closely corresponding to R^2 was defined (21)

$$\text{pseudo} - R^2 = 1 - \frac{SS_{\text{residual}}}{SS_{\text{corrected}}} \quad (5)$$

In addition, residual plots were checked for the absence of trends or correlations. Normality of residuals was evaluated based on the Shapiro–Wilk statistic W , which is calculated for the null hypothesis that the input values are a random sample from a normal distribution. When $\text{Pr} < W$ is smaller than 0.05, the null hypothesis is rejected at a 5% significance level (22). The “bias” of the prediction of the model was graphically evaluated by a scatterplot of the observed vs the predicted values. If the model is appropriate for the data, the data points roughly follow the line of equity (i.e., with a slope of 1).

RESULTS AND DISCUSSION

Relative Reactivity of the Sugars. The AA formation in the asparagine–fructose and –sucrose model systems relative to the formation in the asparagine–glucose model system at each temperature studied is given in **Table 1**. This table, however, gives only a general notion on the difference in relative reactivity of the sugars at different temperatures and does not take the combined effect of temperature and heating time into account. At 140 °C and to a lesser extent at 160 °C, glucose and fructose appeared to generate a similar amount of AA. Overall, the reactivity of the sugars in the AA formation reaction decreases from glucose over fructose to sucrose and with increasing temperature. From a chemical point of view, aldohexose sugars are generally more reactive than ketohexose sugars, explaining the higher amounts of AA formed with glucose as with fructose. The lower AA yields from sucrose as compared to glucose and fructose can be attributed to the fact that sucrose is a nonreducing sugar and, as such, cannot react with asparagine directly to form AA but first needs to undergo decomposition to reactive carbonyl compounds. Decomposition of sucrose will be enhanced at higher temperatures. Nevertheless, no increase in relative reactivity of sucrose is observed at higher temperatures. Despite the fact that hydrolysis of sucrose results in a molar ratio of sugar to amino acid of 2:1, AA formation from sucrose remains 40–50% relative to AA formation from glucose at higher temperatures. In terms of molar ratio, however, a 0.5 to an equimolar ratio of asparagine to glucose is reported to be favorable for AA formation (15, 23).

In literature, different observations are reported concerning the relative reactivity of the sugars for generating AA. Stadler et al. (12) investigating the role of different carbohydrates in the formation of AA observed D-fructose, D-galactose, lactose, and sucrose to release AA with comparable yields in model

reactions with asparagine heated at 180 °C. Becalski et al. (23), on the other hand, observed a lower relative yield of AA from a dry asparagine hydrate–sugar system when sucrose (0.48) was used as compared to glucose (1) and—in contrast to our observations—a higher AA yield (1.8) when fructose was used. Also, in the model experiments of Biedermann et al. (24), fructose appeared to be twice as effective in promoting AA formation as glucose when added to dry potato (5%) and heated at 150 °C for 30 min. Likewise, Ashoor and Zent (25) measuring browning in an amino acid–sugar model system (1:1, pH 9) observed higher browning with fructose as compared to glucose. Sucrose did not yield detectable browning, probably because the disaccharide was not hydrolyzed under the conditions studied (121 °C/10 min). Yaylayan et al. (26), on the other hand, performing model studies at high temperatures by pyrolysis–GC–MS, found sucrose to be significantly more efficient as glucose or fructose in forming AA with asparagine at 350 °C.

The difference between observations can be partly explained by an influence of both temperature and time on the relative activities of sugars toward the production of AA, indicating the importance of kinetic data. However, also, other factors such as the pH and the physical state of the system can influence the relative reactivity of AA precursors. The latter was demonstrated by Robert et al. (27) who monitored on-line AA formation in equimolar asparagine–sugar mixtures by proton transfer reaction mass spectrometry. Under low-moisture conditions, the molecular mobility of the AA precursors appeared to be the determining factor, which is linked to the melting behavior and the release of crystallization water of the reaction system. A melting point of 126 °C was measured by DSC for D-fructose and of 157 °C for D-glucose (27). Sucrose has a melting point of 190–192 °C (with decomposition) (28). In liquid systems, the molecular mobility is no longer a limiting factor and the relative reactivity of the sugar will be determined by its chemical reactivity. This largely explains the discrepancy between our results and those reported in the literature, since most studies reported are performed in dry systems.

In addition, the relative rates of browning of glucose and fructose are reported to depend on the extent with which the reaction mixture is buffered. In unbuffered media, the rate of browning of fructose with amino acids is reported to be greater than that of glucose, whereas in buffered media, fructose browns more slowly than glucose (29).

AA Formation/Elimination Kinetics. The influence of temperature on the AA concentration has already been demonstrated (11, 23, 30, 31). AA starts to be formed above ~120 °C, and dependent on the model system studied and the duration of heating, the AA yield reaches a maximum around 170–180 °C. Knowledge on the combined effect of heating time and temperature on AA formation, on the other hand, is scarce. **Figure 2A–C** shows the AA formation in the asparagine–glucose/fructose/sucrose model systems heated at different temperatures for different treatment times. After prolonged heating, a decrease of the AA content was observed, which can be attributed to AA elimination becoming predominant over AA formation. AA is mainly reactive through its double bond and can react as an electrophile by 1,4-addition to nucleophiles such as SH– or NH₂–groups in biomolecules. AA can thus readily react with various other components present or formed in the food or model system (15). The elimination of AA is also ascribed to AA degradation or polymerization (32).

AA formation and elimination was modeled by means of a second- and a first-order reaction, respectively, but also by two first-order reactions. Both candidate kinetic models appeared

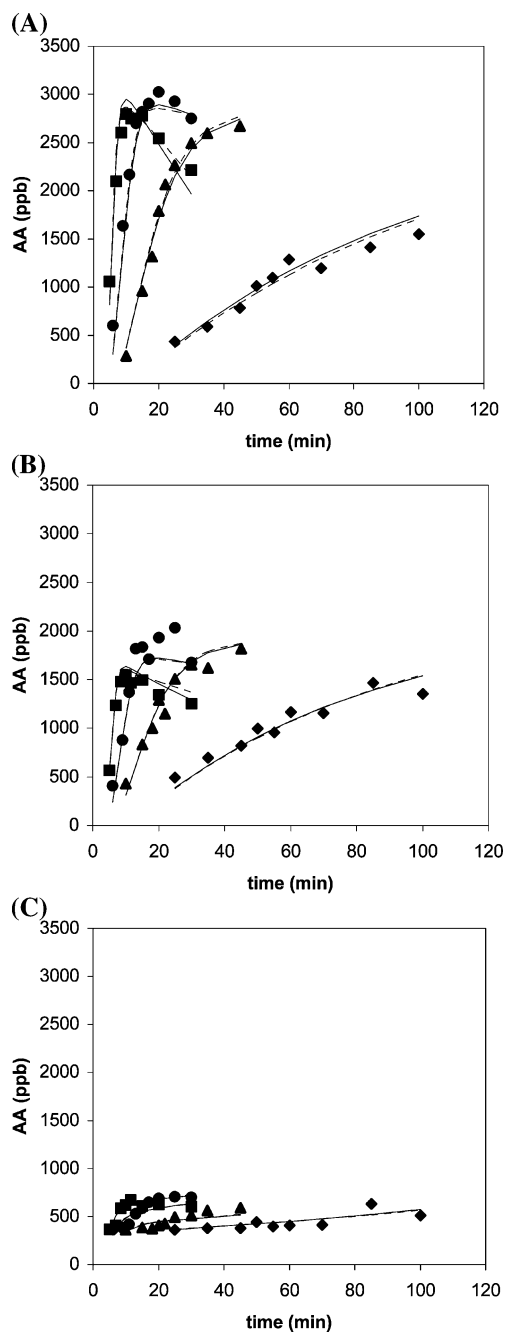


Figure 2. Net formation of AA as a function of heating time at 140 (◆), 160 (▲), 180 (●), and 200 °C (■) in an equimolar model system (0.01 M, pH 6) consisting of asparagine and (A) glucose, (B) fructose, and (C) sucrose. The full and broken lines connect the AA values predicted by the second-order formation/first-order elimination and by the first-order formation/first-order elimination kinetic model, respectively.

to describe the net formation of AA in the model systems accurately, as indicated by the good fit of the model on the data (Figure 2A–C) and confirmed by the high correlation between observed and predicted AA concentrations (Figure 3A–C). It is of course clear that the actual reaction mechanism of AA formation is much more complicated. However, the remarkable good fit suggests that the rate-determining step in the cascade of formation and elimination reactions is a bimolecular (second-order) reaction or a bimolecular reaction with one reactant in large excess (pseudo-first-order) and a monomolecular (first-order) reaction, respectively.

On the basis of the temperature–time profile and AA value of each sample, the reaction rate constants k_{Fref} and k_{Eref} and

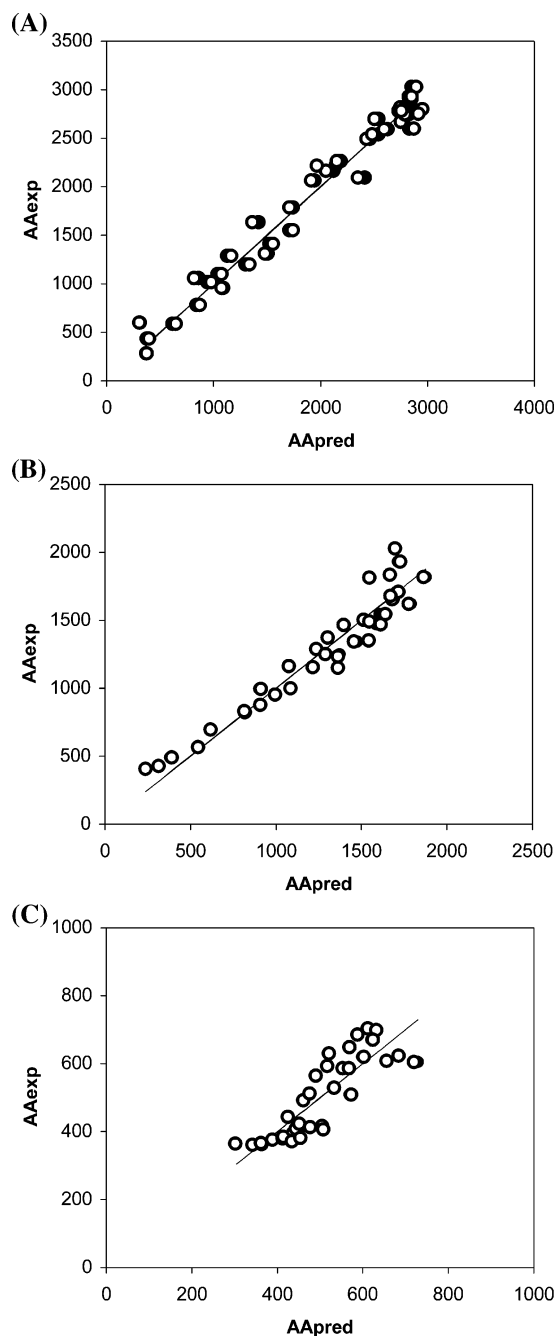


Figure 3. Scatter plot of observed AA values (ppb) and AA values (ppb) predicted by the second-order formation/first-order elimination (○) and by the first-order formation/first-order elimination (●) kinetic model in an equimolar model system (0.01 M, pH 6) consisting of asparagine and (A) glucose, (B) fructose, and (C) sucrose. Full lines have a slope of 1.

the activation energies E_{aF} and E_{aE} could be calculated by nonlinear regression. The kinetic parameters together with their SEs are summarized in Table 2. Kinetic parameters were similar for both candidate kinetic models. Although they have different units, the k_{Fref} values differed approximately by a factor of 10^2 , which can be explained by the fact that it concerns a second-order reaction at one hand and a first-order reaction at the other hand. On the basis of results and evaluation of the kinetic models, one model cannot be considered superior to the other. Nevertheless, considering the argumentation given under Data Analysis and because of its simplicity, the first-order formation/first-order elimination kinetic model seems to be favorable.

The approach used in this paper is a rather pragmatic one, in which the overall formation kinetics are considered rather than

Table 2. Kinetic Parameters^a Describing AA Formation/Elimination in Equimolar Asparagine–Sugar Model Systems (0.01 M, pH 6) Heated between 140 and 200 °C

$T_{\text{ref}} = 160\text{ °C}$	glucose	fructose	sucrose
second-order formation/first-order elimination			
$k_{\text{Fref}} (\times 10^{-3} \text{ M}^{-1} \text{ min}^{-1})$	42.90 \pm 2.33 ^a	30.20 \pm 2.27 ^b	63.40 \pm 22.50 ^{a,b}
$k_{\text{Eref}} (\times 10^{-3} \text{ min}^{-1})$	105.0 \pm 9.2 ^a	111.0 \pm 12.4 ^a	508.4 \pm 130.6 ^b
$E_{\text{aF}} (\text{kJ/mol})$	161.06 \pm 3.84 ^a	139.10 \pm 5.37 ^b	48.88 \pm 3.23 ^c
$E_{\text{aE}} (\text{kJ/mol})$	157.33 \pm 4.68 ^a	148.23 \pm 6.57 ^a	26.47 \pm 1.40 ^b
pseudo- R^2	0.969	0.917	0.734
$\text{Pr} < W$	0.634	0.644	0.475
first-order formation/first-order elimination			
$k_{\text{Fref}} (\times 10^{-3} \text{ min}^{-1})$	0.451 \pm 0.023 ^a	0.303 \pm 0.024 ^b	0.601 \pm 0.214 ^{a,b}
$k_{\text{Eref}} (\times 10^{-3} \text{ min}^{-1})$	111.1 \pm 8.9 ^a	111.4 \pm 13.1 ^a	508.7 \pm 138.9 ^b
$E_{\text{aF}} (\text{kJ/mol})$	168.25 \pm 3.80 ^a	140.81 \pm 5.84 ^b	48.50 \pm 3.15 ^c
$E_{\text{aE}} (\text{kJ/mol})$	167.21 \pm 4.30 ^a	151.91 \pm 7.04 ^a	26.95 \pm 1.53 ^b
pseudo- R^2	0.975	0.912	0.729
$\text{Pr} < W$	0.934	0.619	0.611

^a Values of the same parameter with a different letter are significantly different based on 95% asymptotic confidence intervals. Number of data points = 35; pseudo- $R^2 = 1 - \text{SS}(\text{residual})/\text{SS}(\text{corrected total})$.

details of the complex chemistry. Nevertheless, use of a simple reaction order for complex formation pathways can be useful for modeling chemical changes during processing, when knowledge of pure chemistry or mechanism of the reaction is of less importance. By means of multiresponse modeling, more than one reactant can be followed and modeled. In this approach, various reaction steps (reactants, intermediates, and products) are monitored to gain insight in the reaction mechanism. Recently, Wedzicha et al. (10) presented a kinetic model for the formation of AA in potato and rye products by multiresponse modeling of reducing sugar, amino acid, asparagine, and AA concentrations with time. The kinetic mechanism features a rate-limiting intermediate and additional reaction steps of this intermediate, which are competitive with respect to AA formation. Similarly to our model, a pathway representing physical and/or chemical loss of AA accounts for the reduction of AA measured at high temperatures or long reaction times. Knol et al. (9) proposed a kinetic model for AA formation/elimination in an aqueous asparagine–glucose model system by multiresponse modeling as well, in which AA was considered as an intermediate of the Maillard reaction.

Irrespectively of the kinetic model considered, correlation coefficients between k_{Fref} and k_{Eref} and between E_{aF} and E_{aE} were high (0.94 and 0.74–0.83, respectively) for the model systems with glucose and fructose. In the model system with sucrose, a high correlation was observed between k_{Fref} and k_{Eref} as well (~ 0.94) but also between E_{aF} and k_{Fref} and k_{Eref} (~ 0.78). The correlation between parameters is a consequence of the process of measuring dependent variables at a finite number of data points over a limited range of the independent variable and the subsequent fitting process. The correlation coefficient does not give information about possible relationships in the chemistry or about the physical relationships between parameters (33). If the correlation is high, it may be that a parameter is redundant, that the data points do not span a sufficiently wide range of x values, or that too few data points have been collected (34).

The activation energies quantifying the temperature sensitivity of the AA formation and elimination in the asparagine–glucose and –fructose model systems are around 140–160 kJ/mol. On the basis of asymptotic 95% confidence intervals, the kinetic parameters describing AA formation in the asparagine–glucose and in the asparagine–fructose model system differed significantly, whereas kinetic parameters describing the AA elimina-

tion were similar. Correspondingly, Biedermann et al. (24) observed a similar elimination of D₃-AA at 150 °C for 30 min when glucose or fructose was added to a dry potato model system. AA thus seems to be formed more rapidly and to be more temperature sensitive when asparagine reacts with glucose as compared to fructose. Because AA elimination proceeds similarly, a higher net content of AA is generated in the model system with glucose.

When sucrose is the reactive sugar in the system, the rate constant of the AA elimination is significantly higher as compared to the other two model systems studied, which corresponds to a lower AA yield. Activation energies for AA formation and elimination are significantly lower implying that the rates of AA formation/elimination are not highly affected by a change in temperature. The model, however, does not take into account the hydrolysis of sucrose to glucose and fructose. The difference in kinetic parameter values with the ones estimated for the two other model systems can be due to the fact that other reaction steps in the process are rate determining. Nevertheless, the ratio $k_{\text{Fref}}/k_{\text{Eref}}$ increases from the model system with sucrose over the one with fructose to the one with glucose, which correlates with an increased reactivity of the sugars in the AA formation reaction.

For all three systems studied, k_{Eref} was much higher than k_{Fref} . This does not necessarily indicate that the elimination of AA proceeds much faster than the formation. Next to the relative AA formation and elimination reaction rate constants, the extent of AA formation and of AA elimination depends on the amount of “precursors” available for the reaction. First, a sufficient level of AA and possibly also of other reaction products must be formed before elimination can predominate over formation. In the asparagine–sugar model systems, numerous reactions of, for example, Maillard and caramelization occur, which depend on the nature and the molar concentration of the precursor sugar and which could determine the extent of the AA elimination reaction.

Biedermann and Grob (35) studying AA elimination by D₃-AA at temperatures between 120 and 200 °C observed an increased elimination above 160 °C when 40% sucrose was added to wheat flour. It was suggested that the enhanced elimination at higher temperatures might be due to decomposition products of sucrose. The addition of fructose increased the AA elimination as well but to a higher extent than sucrose and already at 120 °C.

Figure 4 depicts the temperature dependency of the reaction rate constants k_{F} and k_{E} in the different model systems and is based on eq 4. Arrhenius curves related to the AA elimination are similar in the glucose and fructose model systems, whereas Arrhenius curves of AA formation in both systems intersect around 140 °C. Below this temperature, the relative reactivity of the sugars will change, assuming extrapolation of results. The low E_{a} values associated with AA formation/elimination in the sucrose model system are reflected by the nearly horizontal Arrhenius curves.

Note that AA kinetics were studied in a buffer to eliminate as much as possible variation between the model systems studied and a change of pH due to reactions taking place. The rate of the Maillard reaction (and consequently of the AA formation reaction) depends on the rate at which the sugar ring opens to the reducible, open-chained form, which increases with increasing pH (29). In the Maillard reaction, H⁺ ions are formed that decrease the pH of the system. As the pH falls, the rate of the Maillard reaction thus decreases (the optimum pH for the Maillard reaction is >7). A drawback of using a buffer is that

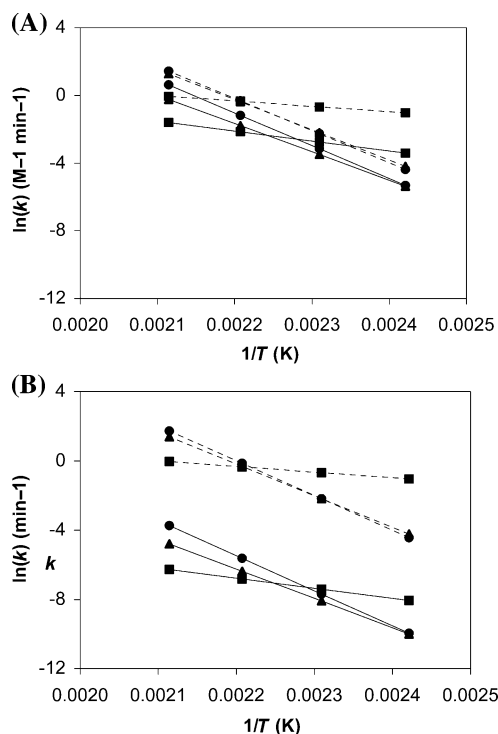


Figure 4. Arrhenius plot of AA formation (full line) and elimination (broken line) in equimolar model systems (0.01 M, pH 6) consisting of asparagine and glucose (●), fructose (▲), or sucrose (■) based on (A) second-order formation/first-order elimination kinetics and (B) first-order formation/first-order elimination kinetics.

buffers can affect the rate of browning. Particularly phosphate buffer, a buffer mostly used to control the pH during the Maillard reaction, has been shown to increase browning and glycine or glucose loss with increasing concentration at pH 5.6 and 100 °C or at pH 7 and 25 °C (36, 37). No glycine loss or browning was observed at pH 7 and 25 °C when citrate buffer was used (36). At pH 3.5 and 121 °C, on the other hand, a higher browning was observed when citrate buffer was used as compared to phosphate buffer (38). The acceleration of the Maillard reaction in the presence of buffers can be explained by the buffer reducing the fall in pH value under alkaline conditions and by an interaction of the buffer with the reactants of the Maillard reaction, but more research on this topic is needed. Remark that the extent of the effect of the buffer on the Maillard reaction rate depends on the temperature as well as on the pH studied. The effect of the buffer ions on the Maillard reaction rate, however, can be of practical importance since food usually contain sugars, amino acids, and both phosphates and organic acid salts.

In this paper, AA kinetics was identified by means of simplified model systems. However, not only the nature of the reactants but also the molar ratio, the a_w , the food matrix, the heating equipment, etc. will influence the AA content in products. Factors influencing the AA content and AA kinetics are interrelated. To obtain a full characterization of AA, the formation/elimination rate needs to be quantified not only in terms of temperature but also in terms of reaction variables such as pH, a_w , concentration of reactants, etc. A next step involves the extrapolation of kinetics from model systems to in situ conditions or real food products.

Before altering processes or foodstuffs to decrease the AA content, the impact of the modification on other food safety issues (e.g., microorganisms and mutagens) and on food quality (e.g., color, odor, flavor, and texture) should be considered. This

only becomes feasible by combining AA formation/elimination kinetics with kinetic data of safety and quality aspects.

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