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Kinetics of formation of acrylamide and Schiff base intermediates from asparagine and glucose

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Abstract

From the concentration of glucose and asparagine as reactants and of acrylamide as product each determined by LC–MS during reaction in an acetonitrile/water (68:32) model system at pH 7.6 (0.04 M phosphate buffer) and from the relative concentration of the Schiff base intermediate, the decarboxylated Schiff base intermediate, the Amadori product and aminopropionamide determined in the same reaction mixtures at 120 °C, 140 °C, 160 °C and 180 °C for up to 16 min, the energy of activation for formation of the Schiff base intermediate was found to have the value 50 ± 2 kJ mol^{-1}, while the apparent activation energy for formation of acrylamide was 64.4 ± 0.6 kJ mol^{-1}, for formation of the decarboxylated Schiff base intermediate 92 ± 2 kJ mol^{-1}, and for formation of the Amadori compound 59 ± 4 kJ mol^{-1}, respectively. At high temperature conditions, formation of the Schiff base is accordingly rate determining, while at lower temperatures, decarboxylation becomes rate determining. Aminopropionamide was only detected at reaction times at which acrylamide formation already is significant in favor of, a reaction path including direct formation of acrylamide from the decarboxylated Schiff base, rather than including dissociation of ammonia from aminopropionamide.

Keywords: Acrylamide; Schiff base; Kinetics; Activation energies

1. Introduction

Formation of acrylamide has, after the discovery of this neurotoxic and carcinogenic compound in processed food by Swedish researchers in April 2002, for the past five years been investigated in various model systems and in foods (IARC, 1994). The highest content of acrylamide is found in food such as French fries and potato chips. The main precursor for acrylamide in food has been found to be asparagine together with various carbonyl compounds, which when present together leads to formation of acrylamide during heat-treatment at temperatures above 120 °C (Mottram, Bronislaw, & Wedzicha, 2002; Stadler et al., 2002). This pathway for formation of acrylamide has been confirmed in several studies (Stadler et al., 2004; Yaylayan, Wnorowski, & Locas, 2003; Zyzak et al., 2003), but other pathways involving precursors such as acrolein and acrylic acid have also been suggested to contribute to acrylamide formation in food (Mottram et al., 2002; Stadler et al., 2002; Yasuhara, Tanaka, Hengel, & Shibamoto, 2003; Zyzak et al., 2003). Formation of acrylamide from asparagine has been linked to the Maillard reaction involving a cascade of reactions with different highly reactive intermediates. Among the proposed intermediates are the Schiff base formed early in the Maillard reaction as the result of elimination of water from the conjugate of glucose and asparagine (Stadler et al., 2004; Zyzak et al., 2003). The breakdown of the Schiff base to acrylamide involves a decarboxylation, followed by decomposition directly to acrylamide and an imine, or followed by hydrolysis to aminopropionamide and carbonyl compounds including glucose. Aminopropionamide have

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further been suggested to eliminate ammonia and be converted into acrylamide (Stadler et al., 2004; Zyzak et al., 2003). Granvolg and Schierberle (2006) have further found 3-aminopropionamide to be a transient intermediate leading to acrylamide.

The activation energy, E_a, for formation and for elimination of acrylamide has been determined with focus on the influence of parameters such as pH and water activity on E_a. While such apparent activation energies clearly are composite quantities, E_a for the individual reaction steps leading to various intermediates and finally to acrylamide are not known. A kinetic description of formation of the intermediates in the reaction sequence leading to acrylamide would improve the understanding of the mechanism leading to acrylamide, which further could help to develop methods to limit acrylamide formation in food. Such mechanistic understanding could more specifically be used to reduce formation of precursors early in the reaction path leading to acrylamide. The Maillard reactions are indeed very complex, and even the more well-studied initial reaction steps have been difficult to describe kinetically, mainly because the Schiff base is difficult to determine quantitatively. However, an improved understanding of the kinetics of the individually steps will lead to better possibilities for more effective control of acrylamide formation in food still with optimal color and flavor formation.

The aim of the present study was to determine the reaction kinetics of formation of acrylamide and formation and decay of precursors and important reaction intermediates in a homogeneous model system containing glucose and asparagine at neutral pH in order to estimate the rate of formation of key intermediates and of acrylamide, and from the temperature dependence also to determine apparent activation energies for the individual steps leading to acrylamide.

2. Materials and Methods

2.1. Chemicals

HPLC grade acetonitrile were obtained from Romil, Cambridge, UK. All other chemicals were obtained from Merck, Darmstadt, Germany, and were of analytical grade. Molecular sieves (3 Å, 3.2 mm pellets) were from Aldrich Chemical (Milwaukee WI 53233, USA). Water purified on a MilliQ purification train (Millipore, Waters, France) was used throughout. Acrylamide is a carcinogen in rodents and classified as a probable human carcinogen and should be handled carefully.

2.2. Preparation of samples

Glucose (0.20 mol/L) and 0.080 mol/L asparagine were dissolved in 10 mL 62:38 acetonitrile/aqueous phosphate buffer with pH 7.6 with a total phosphate concentration of 0.04 M. 30 μL of the sample was transferred to 300 μL HPLC vials, which after sealing were heated in an oven at 120 °C, 140 °C, 160 °C, or 180 °C and after a preset reaction time directly cooled in an ice/water bath until LC–MS analysis. The higher the reaction temperature, the faster the sample became dark brown and later black, indicative of Maillard reactions, and the reaction time was adjusted accordingly for the individual heating temperatures.

2.3. Analysis

High performance liquid chromatography analyses were performed on an Agilent Technologies model 1100 liquid chromatograph equipped with a photo-diode array detector (Agilent Technologies, Wallbronn, Germany). An Aqua, 5 μm, C 18, 150 × 3.00 mm column obtained from Phenomenex (Aschaffenburg, Germany) was used for separation. The flow rate was 0.4 ml/min and eluents were A: 10 mM ammonium acetate, and B: acetonitrile. Solvent programming was isocratic for 100% A for 3 min followed by a linear gradient up to 90% B to 8 min, and isocratic for 90% B in 2 min. The oven temperature was 40 °C. Positive ion electrospray mass spectra were obtained with either an Agilent Technologies MSD 1100 mass spectrometer, operated in the full scan mode, or with an Agilent Technologies ion trap mass spectrometer operated in MSn mode. Both mass spectrometers were equipped with an electrospray interface (Hewlett Packard, Wallbronn, Germany). The following interphase settings were used: nebulizer pressure 40 psi; drying gas 10 l/min, 350 °C; capillary voltage 4000 V.

2.4. Calculations

The rates of formation of the Schiff base, the decarboxylated Schiff base, aminopropionamide and acrylamide were calculated by linear regression of the initial part of a plot of the integrated relative intensity versus t (min) and accordingly expressed as relative concentration per minute, since response factors could only be determined for stable products and not for unstable intermediates. The effect of temperature on reaction was parameterized according to the Arrhenius equation using the relative reaction rates rather than the rate constants: $\text{rate} = \text{rate}_{\text{ref}}\exp(E_a/R(1/T_{\text{ref}} - 1/T))$ to yield the activation energy E_a (J/mol). E_a for formation of the Schiff base, for formation of the decarboxylated Schiff base, and for formation of acrylamide was estimated numerically by linear regression of a plot of ln (rate) versus $1/T$.

3. Results

The acetonitrile/water reaction mixtures of asparagine and glucose were all analyzed by LC–MS and from the chromatograms it was possible to monitor the disappearance of asparagine and glucose, and to monitor the formation of the Schiff base intermediate, the decarboxylated Schiff base intermediate, aminopropionamide and acrylamide (Fig. 1). The identification and quantification

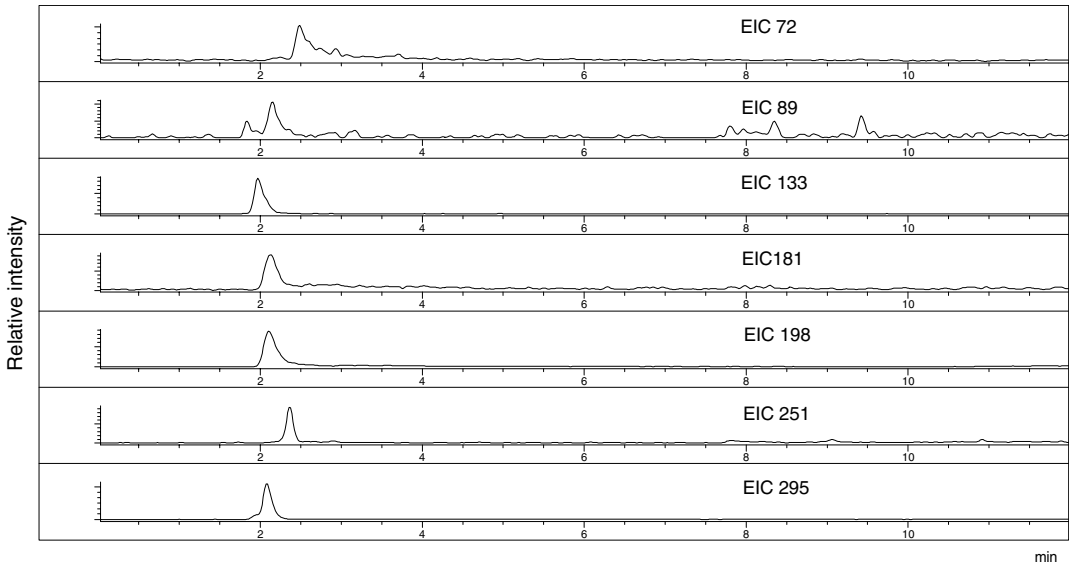

Fig. 1. EIC chromatograms (EIC = Extracted Ion Chromatogram) of acrylamide (MW 71) aminopropionamide (MW 88), asparagine (MW 132), glucose (MW 180), the decarboxylated Schiff base intermediate (MW 250), the Schiff base intermediate (MW 294) and the Amadori compound (MW 294) with MS detection. All compounds are detected at $m/z = [M+H]^+$. For glucose, $[M+NH_4^+]^+$ at m/z 198 is used in addition to 181. The separation procedures were applied separately for each of the compounds either for pure compounds dissolved in the reaction medium (glucose, asparagine and acrylamide) or for the reaction mixtures optimized to yield maximum concentration (aminopropionamide, the decarboxylated Schiff base intermediate, the Schiff base intermediate and the Amadori compound).

of glucose, asparagine and acrylamide were based on external standards, whereas the other compounds were identified by their masses. The Schiff base intermediate and the Amadori compound of asparagine and glucose both has a mass of 295 and can accordingly not be distinguished solely by their mass. The EIC (EIC = Extracted Ion Chromatogram) chromatogram of the mass 295 gave rise to a double peak in the chromatograms of most of the measured samples. The first of these two peaks with mass 295 and accordingly with the shortest retention time was suggested to be the Schiff base whereas the second peak with mass 295 and with the longest retention time was suggested to be the Amadori compound on basis of the following evidence. Reaction of glucose and asparagine in DMSO as a non-aqueous medium together with molecular sieves as water absorbing material resulted in the early eluting 295 peak as the major one. If the reaction was performed in aqueous phosphate buffer with pH 7.6 the later eluting 295 peak was the major one. The Schiff base is generally assumed to be the first stable intermediate of the Maillard reactions in absence of water. Since water is a product of the reaction leading to the Schiff base in an equilibrium process removal of excess water in a non-aqueous system can be used to establish the most favorable conditions for complete conversion to the Schiff base (Hanna, 1966). The Amadori compound of the Maillard reactions has, however, been established as the first stable intermediate in aqueous solutions formed from the Schiff base in the early cascade of reactions, which subsequent leads to 1- and 3-deoxysones, which further degrade to flavor and color compounds (Stadler et al., 2004). Since accumulation of the Schiff base in the non-aqueous DMSO was clearly seen, together with an accumulation of the Amadori compound in the aqueous phosphate buffer (Fig. 2), it became possible to identify both the Schiff base intermediate and the Amadori compound in the reaction mixtures and to quantify the formation of both the Schiff base intermediate and the Amadori compound on a relative scale on basis of the above mentioned assumptions. The peak at m/z 250 can be assigned both the decarboxylated Schiff base (m/z 250) and the decarboxylated Amadori compound (m/z 250), since the decarboxylated Schiff base can rearrange to the decarboxylated Amadori product. The decarboxylated Amadori compound can also produce acrylamide and 3-aminopropionamide, similar to its corresponding

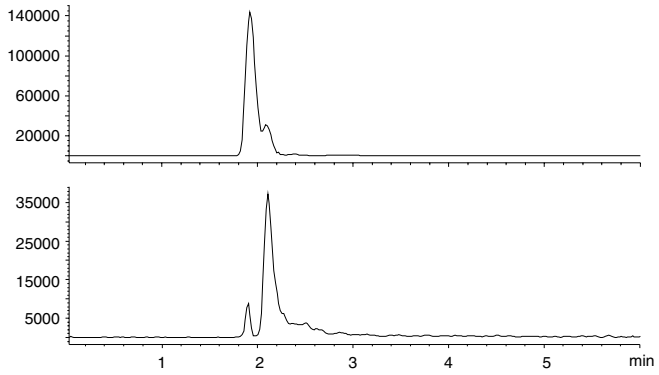

Fig. 2. EIC chromatograms of the initial formed Schiff base intermediate (first part of the peak) and the Amadori compound (second part of the peak) formed from glucose and asparagine in an aqueous phosphate buffer at pH 7.6 (bottom) and in dimethyl sulfoxide (DMSO) (peak) with molecular sieves at room temperature after 3 days of reaction.

decarboxylated Schiff base (Stadler et al., 2004; Zyzak et al., 2003). This peak, however, will be called the decarboxylated Schiff base throughout the paper.

It was not possible to detect the decarboxylated Schiff base intermediate or aminopropionamide at the lowest reaction temperature of 120 °C, at which temperature only acrylamide and the Schiff base intermediate could be detected. At 140 °C aminopropionamide was not detected, although the decarboxylated Schiff base intermediate was detected 2 min after the detection of acrylamide. Aminopropionamide was detected 2 min after acrylamide and the decarboxylated Schiff base intermediate 1 min after the formation of acrylamide at 160 °C. At the highest temperature of 180 °C, the decarboxylated Schiff base intermediate was detected at the same time as acrylamide whereas aminopropionamide again were detected 2 min after acrylamide. The Schiff base intermediate and acrylamide did not reach a concentration maximum at 120 °C within the examined time period for reaction, in contrast to 140 °C, 160 °C and 180 °C, at which temperatures both the Schiff base intermediate and acrylamide was found to have a concentration maximum (Fig. 3).

The initial rate of formation of acrylamide, aminopropionamide, the decarboxylated Schiff base intermediate, and the Schiff base intermediate were estimated by linear regression of the first part of the relative concentration/time plot at each temperature. An example of such an estimation of rate for formation of both acrylamide and the Schiff base intermediate is shown in Fig. 4. The initial rate was preferred to be used in the further calculations in order to minimize any influence of subsequent elimination of acrylamide and further reaction of the intermediates such as the Schiff base intermediate, the decarboxylated Schiff

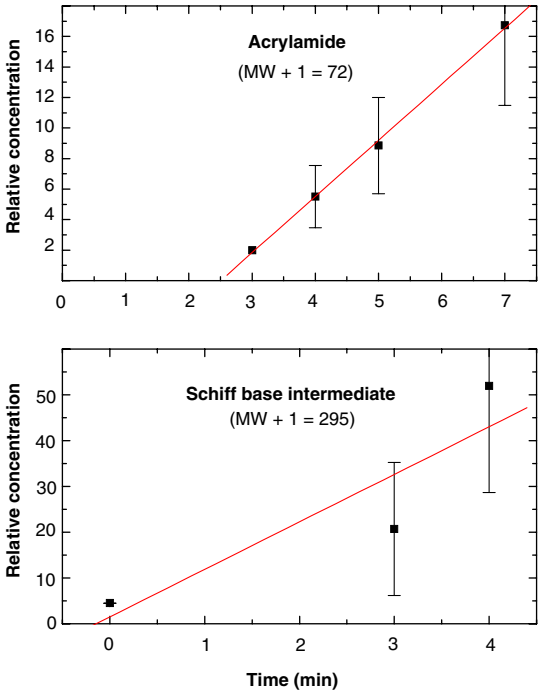

Fig. 4. Initial formation of acrylamide and Schiff base at 140 °C used to estimated the rate of formation of the two compounds in (relative concentration) min^{-1} by linear regression for a 3:1 glucose/asparagine ratio in acetonitrile/water (62:38) solutions of pH 7.6.

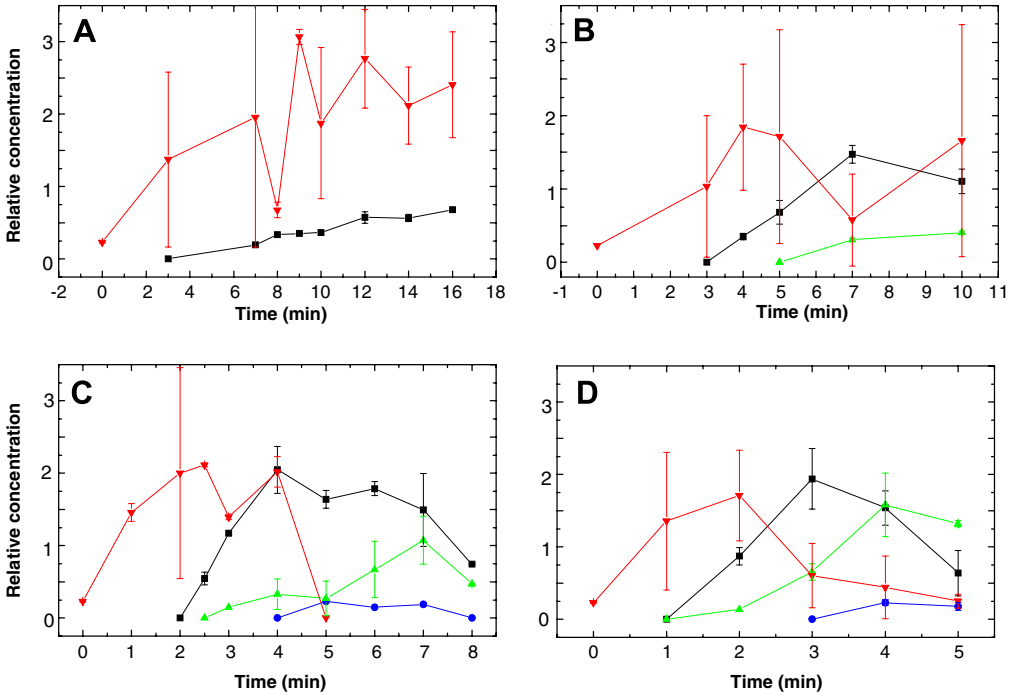

Fig. 3. LC/MS detection of relative concentration of the Schiff base intermediate (MW + 1 = 295 ▼), the intermediate decarboxylated Schiff base (MW + 1 = 251 ▲), aminopropionamide (MW + 1 = 89 ●), and acrylamide (MW + 1 = 72 ■) in acetonitrile/water (62:38) solutions of pH 7.6 at 120 °C (A), 140 °C (B), 160 °C (C) and 180 °C (D).

Table 1
Initial rate (in (relative concentration) min^{-1} with standard deviation) for formation of acrylamide, aminopropionamide, the decarboxylated Schiff base intermediate, the Schiff base intermediate, and the Amadori compound intermediate in an acetonitrile/water (62:38) solution of glucose and asparagine at pH 7.6

	120 °C	140 °C	160 °C	180 °C
Acrylamide (MW 71)	8 ± 1	37 ± 3	92 ± 3	97 ± 21
Aminopropionamide (MW 88)				9 ± 3
Decarboxylated Schiff base (MW 250)		6 ± 0.3	13 ± 2	63 ± 1
Schiff base (MW 294)	17 ± 3	49 ± 8	99 ± 60	127 ± 60
Amadori compound (MW 294)	68 ± 2	286 ± 10	747 ± 11	693 ± 122

All experiments were made in duplicates, see Fig. 3.

base intermediate, aminopropionamide and the Amadori compound leading to the observed steady state concentration seen for some of the reaction conditions. This method of calculation is based on the fact that in the early stage of reaction, acrylamide formation will dominate over reaction of acrylamide with other compounds including addition reactions and polymerization. Notably, it was not possible to convert any of the observed rates to rate constants, since this depends on establishment of reaction order for the individual reactions. However, based on the Arrhenius equation, the energies of activation, E_a, may still be estimated as the first derivative of the rate with respect to temperature. The temperature dependence of formation of acrylamide and of formation of the intermediates accordingly provides information about the energy barriers along the reaction sequence leading to acrylamide. The initial rate of acrylamide formation, of formation of the Schiff base intermediate, and of formation of the decarboxylated Schiff base intermediate increased with increasing temperature as did the parallel formation of the Amadori compound (Table 1). The concentration of asparagine in the reaction mixtures decreased with reaction time as was to be expected, since it is a precursor and accordingly is used up as the reaction proceeds (Fig. 5). The decrease in concentration of glucose during reaction is much less pronounced even at 180 °C, where the rate of asparagine consumption was very high. Glucose was present in the reactions mixtures in a three time excess compared to asparagine, but the expected decrease in glucose concentration corresponding to the disappearance of asparagine at 180 °C was not observed.

E_a of formation of (i) the Schiff base intermediate, (ii) the decarboxylated Schiff base intermediate, (iii) the Amadori compound, and (iv) acrylamide could be estimated from the temperature dependence of the rate of formation of the compounds using the Arrhenius equation. As may be seen from Fig. 6, a reasonable linear dependence of ln (rate) was observed for each of the compounds over the rather large temperature interval of up to 60 °C. The E_a of formation of acrylamide were found to be lower than E_a for formation of the decarboxylated Schiff base intermediate, but it was significantly higher than E_a for formation of both the Schiff base intermediate and the Amadori compound. Decarboxylation of the Schiff base intermediate to yield the decarboxylated Schiff base intermediate had the highest E_a and was larger by a factor of two compared to E_a for formation of the Schiff base intermediate (Table 2). E_a for formation of the Schiff base intermediate was not different from E_a for formation of the Amadori compound.

Two reaction pathways have been suggested for the degradation of the decarboxylated Schiff base intermediate to yield acrylamide, involving either direct decomposition to acrylamide and an imine (MW + 1 = 180), or with aminopropionamide as an intermediate. Degradation of the decarboxylated Schiff base intermediate to aminopropionamide and a carbonyl compound (MW + 1 = 181) has also been suggested to generate acrylamide by elimination of ammonia from aminopropionamide (Fig. 7) (Zyzak et al., 2003). The relative concentration corresponding to the carbonyl compound (MW + 1 = 181) and the imine (MW + 1 = 180) both increased with prolonged heating time at 180 °C as seen in Fig. 8, whereas no significant change in the relative concentration of the carbonyl compound and the imine was noted for the experiments at 120 °C, 140 °C and 160 °C.

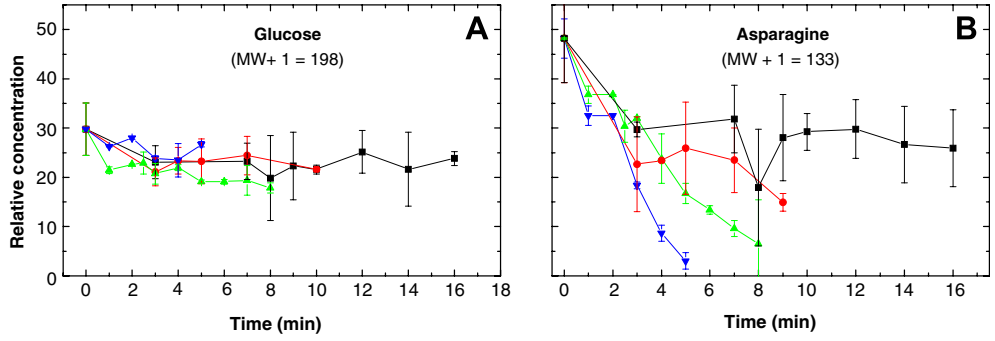

Fig. 5. LC/MS detection of relative concentration of reactants for acrylamide formation (glucose and asparagine in A and B, respectively) during reaction of glucose/asparagine in a molar ratio of 3:1 investigated in acetonitrile/water (62:38) solutions with pH 7.6 at 180 °C (▼), 160 °C (▲), 140 °C (●) and 120 °C (■).

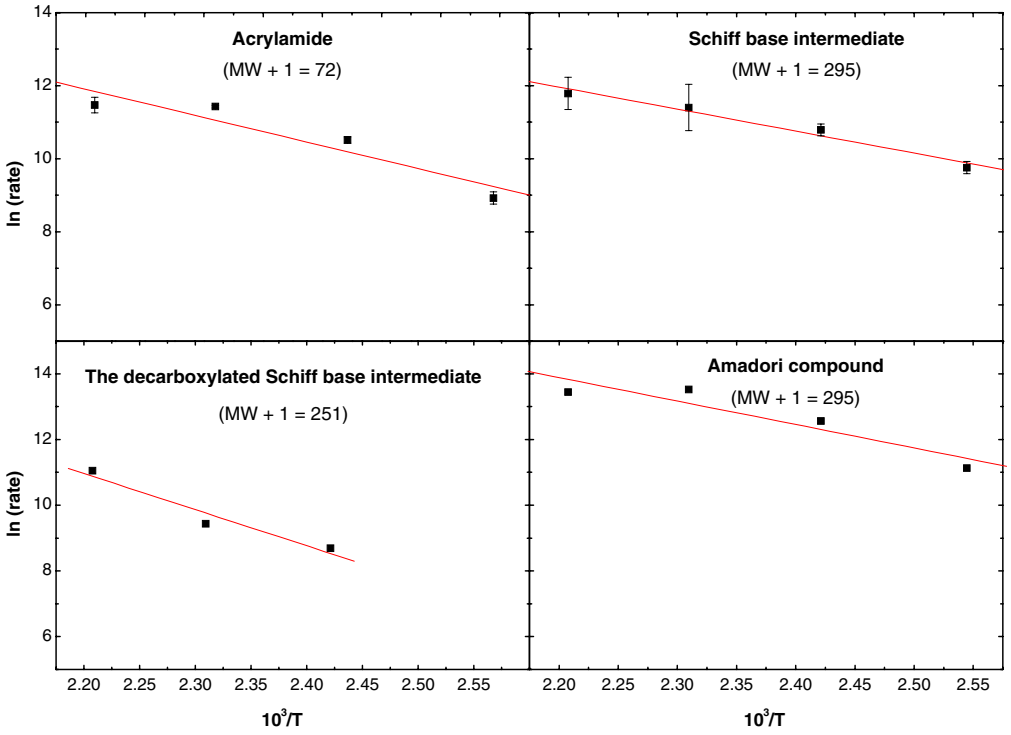

Fig. 6. Arrhenius plot for formation of acrylamide, the Schiff base intermediate, the decarboxylated Schiff base intermediate and aminopropionamide from glucose and asparagine for a glucose/asparagine reactant molar ratio of 3:1 acetonitrile/water (62:38) solutions as estimated from initial rates in (relative concentration)·min^{-1}, see Fig. 4. E_a calculated as $E_a = -$slope R is given in Table 2.

Table 2
Activation energies, E_a, for formation of acrylamide, of the decarboxylated Schiff base intermediate, of the Schiff base intermediate, and of the amadori compound intermediate

Analyte (MW)	E_a (kJ/mol)
Acrylamide (71)	64.4 ± 0.6
Decarboxylated Schiff base intermediate (250)	92 ± 2
The Schiff base intermediate (294)	50 ± 2
Amadori (294)	59 ± 4

The calculation is based on the initial rates of formation in an acetonitrile/water (62:38) solution of glucose and asparagine at pH 7.6 see Table 1. All experiments were made in duplicates, for examples of Arrhenius plots, see Fig. 7.

4. Discussion

Formation of acrylamide as part of the Maillard reactions is initiated by the reaction between asparagine and a carbonyl compound such as glucose to give an *N*-carbonyl conjugate. For glucose dehydration of the *N*-glycosyl conjugate leads to the formation of the corresponding Schiff base. For acrylamide to be formed from the Schiff base a decarboxylation is necessary, followed by further degradation of the decarboxylated Schiff base. This degradation step involves cleavage of a nitrogen–carbon bond, which can occur by two different mechanism involving (i) direct degradation of the decarboxylated Schiff base to acrylamide and an imine, or (ii) involving addition of water to the decarboxylated Schiff base to yield aminopropionamide and a carbonyl compound, as was proposed by Zyzak et al. (2003) and by Stadler et al. (2004).

The temperature dependence of formation of acrylamide has also been used by other researchers to estimate E_a for the gross reaction. However, a direct comparison between values of E_a can be difficult, because variations in composition of the model systems developed and in the approximations used for calculations may both have strong influence on the derived values for E_a. The value of E_a for acrylamide formation is affected among other factors by the water activity (a_w). In a previous study, E_a for acrylamide formation were shown to increase with decreasing a_w with E_a values ranging from 25 to 137 kJ/mol depending both on the molar ratio of glucose and asparagine and on a_w (Hedegaard, Frandsen, Granby, Apostolopoulou, & Skibsted, 2007). The E_a of 64 kJ/mol found for acrylamide formation in the present study agrees with the results obtained previously for high values of a_w and a molar ratio between glucose and asparagine of 1:5. A similar effect of a_w on E_a for formation of the Amadori compound was demonstrated by Eicher, Laible, and Wolf (1985) in a study, where E_a for formation of the Amadori compound was found to have the value 78 kJ/mol at a water content of 12.6%, but increased to 126 kJ/mol for a water content of 2.9%, indicating that decrease in molecular mobility at low a_w increases E_a. Claeys, Vleeschouwer, and and Hendrickx (2005) determined E_a for both formation and elimination of acrylamide in a model system consisting of

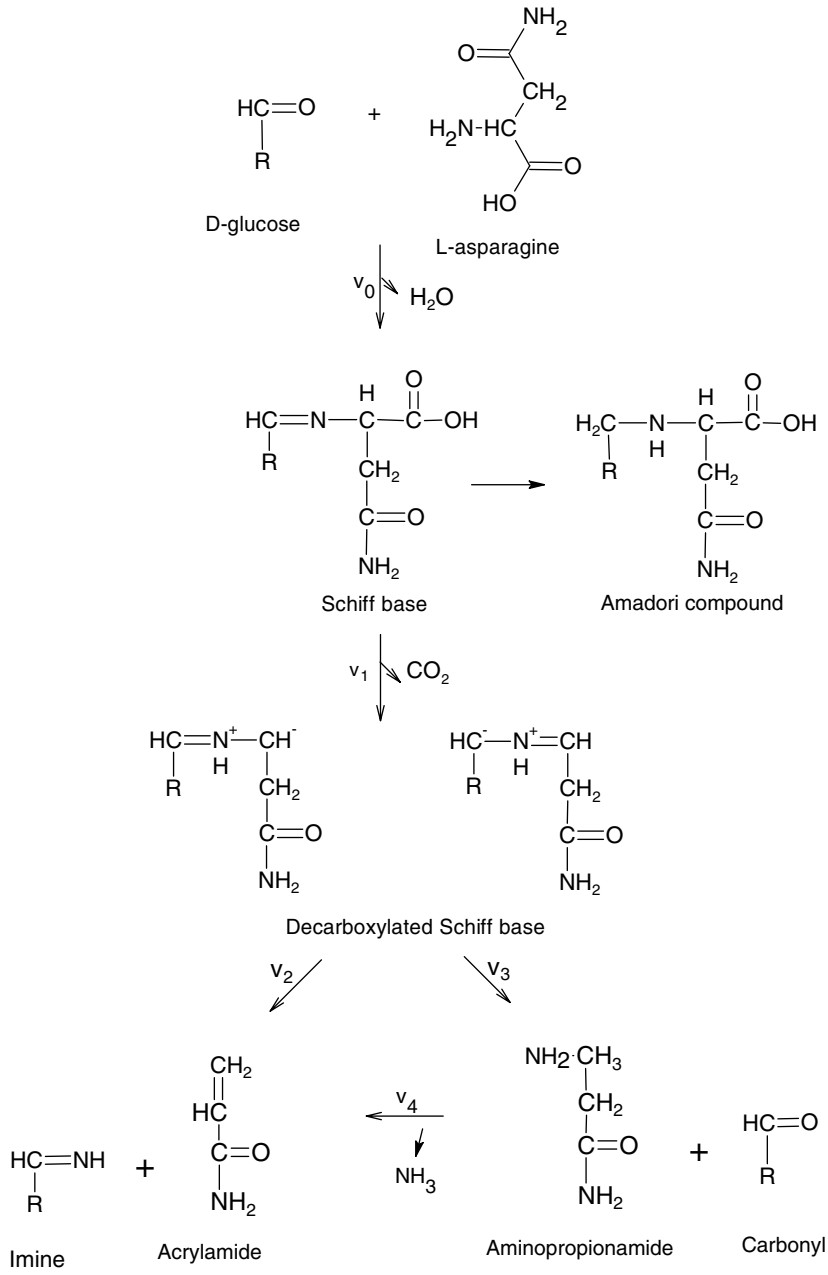

Fig. 7. Reaction scheme for formation of acrylamide from glucose ($R = C_5H_{11}O_5$) and asparagine.

asparagine and different carbonyl compounds such as glucose, fructose, and sucrose in the temperature range 140–200 °C. They found somewhat surprisingly a significantly higher value for E_a for formation of acrylamide at pH 6 from glucose and fructose than from sucrose with values of 49 kJ/mol for sucrose, 140 kJ/mol for fructose and for glucose ranging between 161 and 169 kJ/mol. However, De Vleeschouwer, Van der Plancken, Van Loey, and Hendrickx (2006) found that E_a for formation of acrylamide decreased with increasing pH in an aqueous model system and had values of 208 kJ/mol for pH 4, 191 kJ/mol for pH 6 and 130 kJ/mol for pH 8. Sadd and Hamlet (2005) determined a value of 120 kJ/mol in a model for cereal products. Knol et al. (2005) estimated the E_a of the formation of the Schiff base, melanoidins and acrylamide to be 58 kJ/mol, 94 kJ/mol and 40 kJ/mol, respectively, in an aqueous model system. Although the intermediate Schiff base was not measured directly, but calculated indirectly the value agrees with the value found in the present study. It should, however, be noted that all the reported E_a values are composite quantities, since they were determined for reaction products in a sequence of reactions except for the Schiff base intermediate, which is a primary reaction product (v_0 in Fig. 7). With this reservation still an important conclusion appears from the pattern seen for the energies of activation in Table 2 concerning the rate-determining step for acrylamide formation under different temperature conditions.

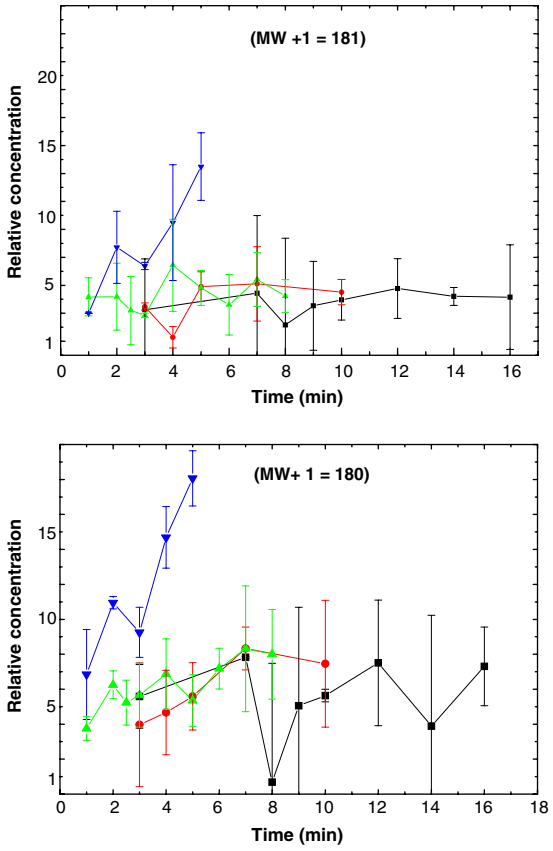

Fig. 8. Relative concentration of the carbonyl compound (MW + 1 = 181) and the imine (MW + 1 = 180) formed when the decarboxylated Schiff base is degraded and (i) the imine is formed (MW + 1 = 180) directly together with acrylamide, or (ii) the carbonyl compound (MW + 1 = 181) is formed together with aminopropionamide as acrylamide precusor at (■) 120 °C, (●) 140 °C, (▲) 160 °C and (▼) 180 °C.

E_a for formation of the decarboxylated Schiff base intermediate (v_1 in Fig. 7) has a higher value than both E_a for formation of the Schiff base intermediate (v_0) and for formation of acrylamide. The higher E_a indicates higher temperature dependence for the decarboxylation of the Schiff base intermediate (v_1) than for the rate of the subsequent formation of acrylamide from the decarboxylated Schiff base intermediate ($v_2 + v_3$). As a consequence of this high E_a for the decarboxylation, the rate of decarboxylation of the Schiff base intermediate (v_1) is lower than the rate of degradation of the decarboxylated Schiff base to acrylamide (v_2 and v_3) at low temperature. The higher rate of degradation of the decarboxylated Schiff base intermediate compared to the formation of the decarboxylated Schiff base intermediate at 120 °C is clearly evidenced by the absence of signal of decarboxylated Schiff base intermediate in the chromatograms as may be seen in Fig. 3. A similar pattern for the energies of activation explains the absence of aminopropionamide in the reaction mixtures at this low temperature. At low reaction temperature, v_1 is accordingly concluded to be lower than v_2 and v_3. For conditions of increasing temperature, v_1 becomes higher than the rates v_2 and v_3, which results in an increasing concentration of the decarboxylated Schiff base intermediate during reaction allowing detection of the decarboxylated Schiff base at 140 °C, at 160 °C and at 180 °C. At higher temperature, v_1 is thus concluded to be higher than v_2 and v_3.

Aminopropionamide was only detected at 160 °C and 180 °C and only for reaction times where the formation of acrylamide already was significant. The absence of aminopropionamide at 120 °C and at 140 °C and the delayed appearance compared to acrylamide at 160 °C and 180 °C together indicates that the direct degradation pathway of the decarboxylated Schiff base to acrylamide and an imine (MW + 1 = 180) is more important for acrylamide formation compared to formation with aminopropionamide as an intermediate under the actual reaction conditions. The relative concentration of the imine detected for reaction at 180 °C was approximately 20 times higher than the detected concentration of aminopropionamide providing further evidence for the importance of the direct reaction to yield acrylamide. A more quantitative comparison of the relative concentration of the carbonyl compound and the imine during reaction is, however, not possible due to the indirect identification by mass only. Another possible reaction for excess of glucose is a reaction between glucose and aminopropionamide, reforming the decarboxylated Schiff base from which acrylamide subsequently is eliminated (Zyzak et al., 2003). The imine may likewise hydrolyze to yield ammonia and a carbonyl compound with the perspective of further reaction with aminopropionamide.

In conclusion, for low temperature conditions, decarboxylation of a Schiff base intermediate is rate determining for acrylamide formation, while at higher temperatures formation of the Schiff base is rate determining. For the conversion of the decarboxylated Schiff base to acrylamide, the direct reaction dominates rather than conversion via aminopropionamide.

Acknowledgments

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