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Mechanism of chemical activation of sodium chloride in the presence of amino acids

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ABSTRACT

Sodium chloride has been shown to promote chlorination of glycerol during thermal processing. However, the detailed mechanism of this reaction is not well understood. Preliminary experiments have indicated that the reaction mixture should contain an amino acid and it should be dissolved thoroughly in water in order to induce chlorination. These observations are consistent with the process of dissociation of sodium chloride and its re-association with amino acid and eventual formation of the chlorinating agent in the form of the hydrochloride salt. Release of HCl from this salt can be manifested in chlorination and hydrolytic reactions occurring during thermal processing. The generation of HCl at room temperature from a mixture of sodium chloride and glycine was confirmed through spectrophotometric monitoring of the pH. Hydrolytic and chlorination reactions were demonstrated through monitoring of formation of HMF and chlorinated products under pyrolytic conditions using glucose or sucrose and amino acid mixtures.

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1. Introduction

Recent interest in reducing the salt content of food has been mainly motivated by its presumed health effects as one of the main risk factors associated with cardiovascular diseases (He & MacGregor, 2009). Very little attention, if at all, has been directed towards its possible chemical role in food or in its ability to chlorinate food components during processing. Various studies (Calta et al., 2004; Hamlet, Sadd, & Gray, 2004) have suggested that salt may react with glycerol and contribute to the formation of chloropropanols (CP) (Hamlet & Sadd, 2009) during processing. Although the generation of CPs and their esters have primarily been associated with the refining process of edible oils, some studies have demonstrated their formation in commercial and domestically processed foods containing sodium chloride (Baer, de la Calle, & Taylor, 2010; Calta et al., 2004; Crews, Brereton, & Davies, 2001; Divinová, Doležal, & Velíšek, 2007; Doležal, Kertisová, Zelinková, & Velížek, 2009; Reece, 2005). Simulated food systems, containing lipids and sodium chloride, have established the ability of salt to generate CPs (Reece, 2005; Velíšek, Calta, Crews, Hasnip, & Doležal, 2003) as well as their esters (Freudenstein, Weking, & Matthäus, 2013; Svejkovská, Doležal, & Velíšek, 2006). Further investigations are needed to characterise the reaction mechanism behind the activation of salt as an effective chlorinating agent as well as its influence on other thermal reactions such as the Maillard reaction (Troise & Fogliano, 2013). Literature regarding the influence of salt on Maillard model systems is generally conflicting and frequently measures the effect of salt only on browning. Experiments performed under controlled pH values (neutral or alkaline) that are known to promote browning (Cerny, Fitzpatrick, & Ferreira, 2011; Kwak & Lim, 2004; Thongraung & Kangsanan, 2010; Yamaguchi et al., 2009) have demonstrated the capacity of salt to hinder non-enzymatic browning. On the other hand, research carried out where the pH was not controlled, such as dry systems, have demonstrated that addition of salt causes increased browning (Moreau, Bindzus, & Hill, 2009a; Moreau, Lagrange, Bindzus, & Hill, 2009b). Using simulated dry cereal model systems Moreau et al. (2009b) have observed a significant increase in browning due to the presence of sodium chloride. Promotion of browning by salt is often associated with either its hygroscopic nature – retaining more moisture in the system, enhancing mobility of Maillard precursors and thereby also the reaction – or its potential as a plasticiser – reducing the glass transition temperature resulting in the extension of a products' time in the rubbery state, i.e. the period of processing where the Maillard reaction is most active. Investigating the potential of salt as a plasticiser as well as its hygroscopic nature, Moreau et al. (2009a) have determined that neither property could be attributed to the effect of salt on browning, leading them to conclude that, "chemical

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changes in the Maillard reaction pathways [may] occur because of the presence of NaCl and KCl, which could explain the impact on colour." While Moreau et al. (2009a) have demonstrated that non-enzymatic browning was enhanced by the presence of salt in dry systems, in a subsequent publication (Moreau et al., 2009b) they, as well as others, have shown that sodium chloride can have a negative correlation with the production of acrylamide (Moreau et al., 2009b; Van der Fels-Klerx et al., 2014) suggesting that the addition of salt has the potential to interfere with the initial stages of the Maillard reaction. Furthermore, Fiore et al. (2012) using encapsulated salt, were unable to observe any correlation between the salt concentration and acrylamide formation in cookie models, indicating that encapsulation actually prevented the participation of salt in any possible chemical reaction. In addition, it has been demonstrated that the salt can hinder the formation of Amadori product (Cerny et al., 2011) and furosine (Yamaguchi, Nomi, Homma, Kasai, & Otsuka, 2012). If sodium chloride can promote chlorination of glycerol, it may do so in other food components. This study aims to explore the role of amino acids in promoting the chemical activity of sodium chloride, in terms of its effect on the acidity and in the subsequent influence it may have on the Maillard reaction and on chlorination reactions in general.

2. Materials and methods

2.1. Chemicals

The following chemicals were used without further purification: asparagine (98%), aspartic acid (98%), arginine (99%), furfuryl alcohol (99%), glutamine (99%), glycidol (96%), glycine hydrochloride (99%), 3-monochloro-1,2-propanediol (98%), 2,3-dichloro-1-propanol (>97%), styrene (⩾99%), threonine (98%), tyrosine (99 + %), tryptophan (99%), proline (99%), phenylalanine (⩾98%), glycine hydrochloride (99%), sodium glycinate (98%), glucose (>99.5%), sucrose (>99.5%), as well as 2,6-dichloroindophenol (DCPIP) sodium salt (98%), were purchased from Sigma–Aldrich (St Louis, MO); 2-chloropropane-1,3-diol (98%) was purchased from Toronto Research Chemicals (Ontario, Canada); oxalic acid (⩾99%) and 1,3-dichloro-2-propanol (98%) was purchased from ACP Chemicals Inc. (Montreal, Quebec, Canada); glycerol (99.5%) was purchased from Fluka (Steinheim, Germany).

2.2. Spectrophotometric determination of pH using 2,6-dichloroindophenol (DCPIP)

DCPIP stock solution (200 μL, 1.24 mM) was added to sodium chloride solution containing glycine (1.6 mL) in either 1:1 or 1:2 M ratios, having final concentration of 2.4 M (1:1) each or 4.8 M with respect to glycine in the case of 1:2 ratio. The solutions were subsequently vortexed for 30 s before immediate analysis (0 min). The absorbance spectra (in the wavelength range of 400–750 nm) were acquired at 0, 10 and 20 min intervals using an Evolution 300 model UV–Vis spectrophotometer (Thermo Electron Corporation) with a bandwidth of 2 nm and a path length of 1 cm using quartz cuvettes. Distilled water was used as the blank solution.

2.3. FTIR analysis

Equimolar mixture of glycine hydrochloride/sodium glycinate (1:1) and of glycine/NaCl (2:1) mixtures were dissolved in water (200 μL), vortexed for 30 s and then heated at 100 °C for an hour until dry. The dry residues were analysed by FTIR and their pH values were measured after the addition of 1.6 mL of distilled water as described above. Infrared spectra were acquired at 30 °C on a Bruker Alpha-P spectrometer (Bruker Optic GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulphate (DTGS) detector and a temperature-controlled single-bounce diamond attenuated total reflectance (ATR) crystal, and a pressure application device for solid samples. Processing of the FTIR data was performed using Bruker OPUS software (Bruker Optic GmbH, Ettlingen, Germany) where the Quick Compare function with a 95% threshold was used to determine similarity between the FTIR spectra.

2.4. Pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS) analysis of model systems containing glycerol

A Hewlett–Packard GC/mass selective detector (5890 series II GC/5971B MSD) interfaced to a CDS Pyroprobe 2000 unit, through a valved interface (CDS 1500), was used for Py–GC/MS analysis of all samples containing glycerol. Glycine and glycerol (1:1) or mixtures containing NaCl at a 2:1 ratio were either immediately prepared for pyrolysis or were reconstituted in a minimal amount of water and subsequently allowed to dry (24 h) at room temperature beforehand. All samples were prepared for pyrolysis by introducing 2.5 mg of the resulting solid samples inside the quartz tube (0.3 mm thickness), which was subsequently plugged with quartz wool and inserted inside a pyrolysis probe. The pyroprobe was set at 250 °C with a total heating time of 20 s. The pyroprobe interface temperature was set at 250 °C. The samples were introduced in splitless mode. The 3 mL/min constant flow was maintained by an electronic pressure controller (Hewlett–Packard). Capillary direct MS interface temperature was 180 °C; ion source temperature was 280 °C. The ionisation voltage was 70 eV and the electron multiplier was 2047 V. The mass range analysed was 17–300 amu. The column was a CP-Sil 5CB (30 m × 0.32 mm × 0.25 μm; Varian, Mississagua, ON, Canada). The column initial temperature (−5 °C) was held for 2 min then increased to 100 °C at a rate of 30 °C/min, then further increased to 250 °C at a rate of 8 °C/min, and held for 35 min.

2.5. Pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS) analysis of model systems listed in Table 1

A Varian CP-3800 gas chromatograph coupled to a Saturn 2000 ion trap detector interfaced to a CDS Pyroprobe 2000 unit through a valved interface (CDS 1500) was also used for Py–GC/MS analysis of model systems (0.5 mg) shown in Table 1. Sugar, amino acid and sugar/amino acid (1:1 M ratio) mixtures were introduced inside the quartz tube (0.3 mm thickness) and glycine hydrochloride was added, as previously described by Rahn and Yaylayan (2013). The temperature of the pyroprobe interface was set at 250 °C. Model systems were initially pyrolysed at 250 °C with a total heating time of 20 s. Samples were left in the interface for a total of 2 min then removed. The initial temperature of the column was set at −5 °C for 5 min and then increased to 50 °C at a rate of 50 °C/min; immediately, the temperature was further increased to 270 °C at a rate of 8 °C/min and kept at 270 °C for 6 min. A constant flow of 1.5 mL/ min was used during analysis. The capillary direct MS interface temperature was 250 °C; the ion source temperature was 175 °C. The ionisation voltage was 70 eV, and the electron multiplier was set at 1500 V. The mass range analysed was 20–650 amu. The column was a fused silica DB-5 MS column (50 m × 0.2 mm i.d. × 0.33 μm film thickness; J&W Scientific). The identity and purity of all chromatographic peaks were determined by using NIST AMDIS software (version 2.1).

Table 1
Model systems[a] studied.

Single carbohydrates			Single amino acids[b]	
Glucose			Arginine	
Glucose + oxalic acid			Asparagine	
Sucrose			Aspartic acid	
Glycidol			Glutamine	
			Phenylalanine	
			Proline	
			Serine[c]	
			Threonine	
			Tryptophan	
			Tyrosine	
Model systems[d]			Targeted compound	
Furanmethanol + glycine hydrochloride			(chloromethyl)furan	
Hydroxymethyl furfural + glycine hydrochloride			(chloromethyl)furfural	
Styrene + glycine hydrochloride			(chloromethyl)benzene	
			(chloroethyl)benzene	
Precursor model systems[e]			Identified products[f]	
Glycidol/glycerol	3-MCPD	2-MCPD	1,3-DCP	2,3-DCP
Glucose/sucrose	2-(Chloromethyl)furan		5-(Chloromethyl)furfural	
Phenylalanine	(chloro)methylbenzene		(chloroethyl)benzene	

[a] All model systems were pyrolysed alone and in the presence and absence of compartmentalised glycine hydrochloride.
[b] All amino acids were pyrolysed in a 1:1 M ratio with either glucose or sucrose in the presence and absence of compartmentalised glycine hydrochloride.
[c] Model system run in the presence of oxalic acid.
[d] Model systems used to pyrolytically generate targeted compounds.
[e] In the presence of glycine HCl.
[f] Identified through comparison of their retention times and mass spectra.

3. Results and discussion

Sodium chloride is viewed as an essential processing ingredient responsible for a variety of quality attributes in many food products. While some of the consequences of adding salt have been characterised (Man, 2007) the chemical fate of sodium chloride in processed food is often neglected despite evidence for its ability to alter the course of the Maillard reaction and to chlorinate glycerol during processing, generating CPs and CP esters. Initial studies were conducted to explore the effect of addition of NaCl on the product distribution during pyrolytic reactions involving amino acids and glycerol. These studies have indicated that when sodium chloride was added to glycerol/amino acid or sugar/amino acid models and subsequently pyrolysed no specific chemical effect was observed relative to the samples lacking salt, both samples generated similar GC/MS profiles. However, when the mixtures were completely dissolved in water and re-analysed after a drying step, the model systems exhibited significant changes in their chemical profiles (see Fig. 1) including the formation of chlorinated species (Fig. 2, Table 2). These observations can only be rationalised if sodium chloride was converted into a chlorinating agent. We hypothesised therefore that one possible chlorinating species that could be formed in the presence of amino acids – the common component in all the model systems studied - is the hydrochloride salt of the amino acid, that is known to release HCl upon heating or upon dissociation in aqueous solutions. Since the chemical effect of the salt appeared after a dissolution/drying cycle, we propose therefore that after the dissociation of sodium chloride and the complete solvation of sodium and chloride ions in water, their respective solvation shells could be penetrated by the polar components in the water such as amino acids and sugars during the evaporation step, forming a barrier that can partially prevent the reformation of NaCl upon evaporation of water and at the same time causing re-association of some of the sodium and chloride ions with different ionic or polar sites in the mixture, such as amino acids and sugars (see Fig. 3), or other ionic species if present, such as phosphates or proteins. This exchange in ionic sites is manifested by the partial conversion of NaCl into a hydrochloride salt of the amino acid within the examined model systems, chemically activating NaCl. Hydrochloride salts of amino acids are known to release gaseous hydrochloric acid upon heating or dissociation in aqueous environments by releasing hydronium and chloride ions. This process not only can cause chlorination during heating of samples containing NaCl and amino acids but can also increase the acidity of the medium. According to the above hypothesis (Fig. 3) when sodium chloride is dissolved in water the zwitterionic form of amino acids can associate with sodium and chloride ions, forming an unstable salt complex (shown in square brackets in Fig. 3), which upon heating can release HCl, enhancing acid-catalysed reactions in the medium, such as formation of HMF or hydrolysis of sucrose as has been observed by Van der Fels-Klerx et al. (2014). In the extreme case of complete loss of HCl to the environment, this process may cause an eventual increase in alkalinity of the remaining residue, due to the presence of sodium salts of amino acids and generation of an equimolar residue of the free amino acid and its sodium salt.

3.1. Monitoring the pH profile of a concentrated aqueous solution of NaCl in the presence of glycine at room temperature

If the premise of the above hypothesis shown in Fig. 3 is correct, then the chemical activation of NaCl in the presence of glycine can be inferred through monitoring the changes in the pH profile of a concentrated glycine/NaCl solution over time, using the pH indicator dye 2,6-dichloroindophenol (DCPIP). This blue dye (λ_{max} 600–610 nm) in aqueous solution is stable over time but changes colour into pink (λ_{max} 520–540 nm) under relatively strong acidic conditions (<pH 4) (Patrick & Svehla, 1977). When concentrated aqueous solutions (4.8 M) of glycine or NaCl alone were monitored over time in the presence of the dye (1.24 mM), as expected they did not show any changes in their absorption profiles and the λ_{max} remained at a value of ~600 nm (blue) in both cases. It is expected therefore that a solution containing both glycine and NaCl to show similar behaviour in the absence of any interaction that alters the pH profile of the solution. To verify this fact, the time-dependent spectra of glycine/NaCl solutions (4.8 M in glycine) were acquired

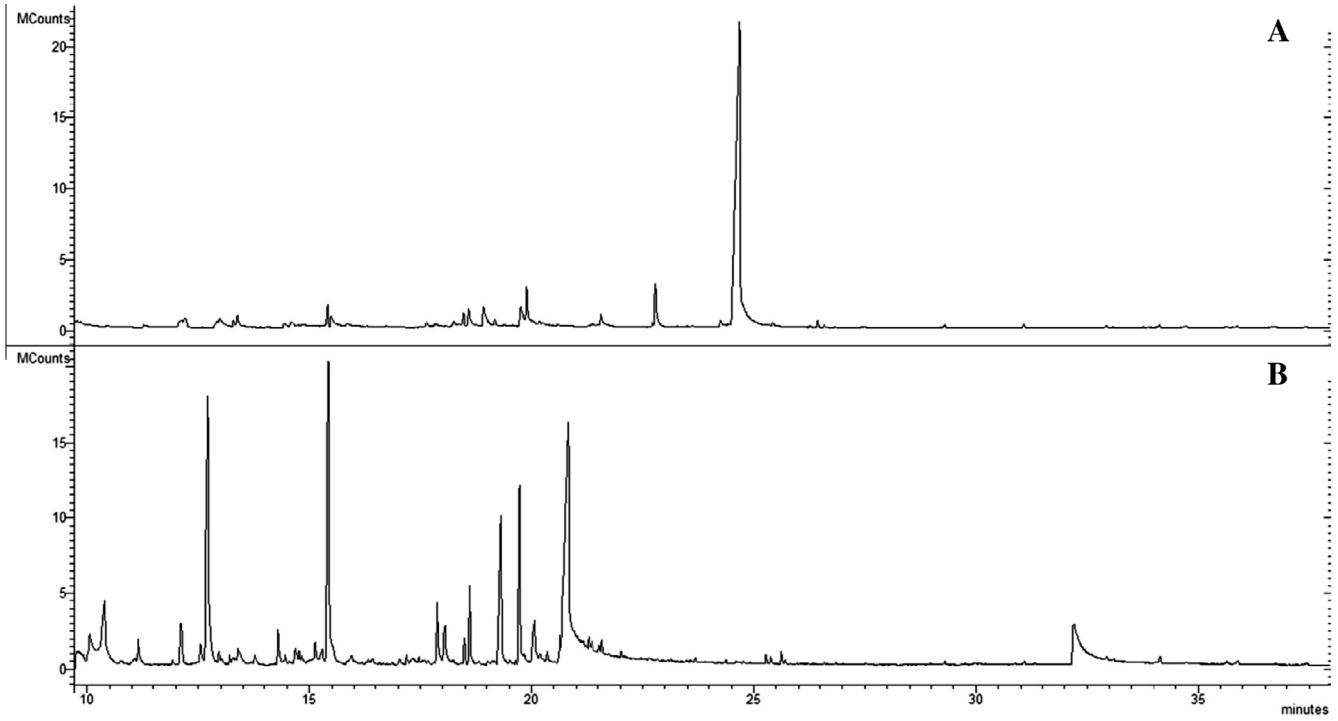


Fig. 1. Comparison of pyrolysis–GC/MS profiles of (A) serine/sucrose model system and (B) serine/sucrose model system in the presence of glycine hydrochloride.

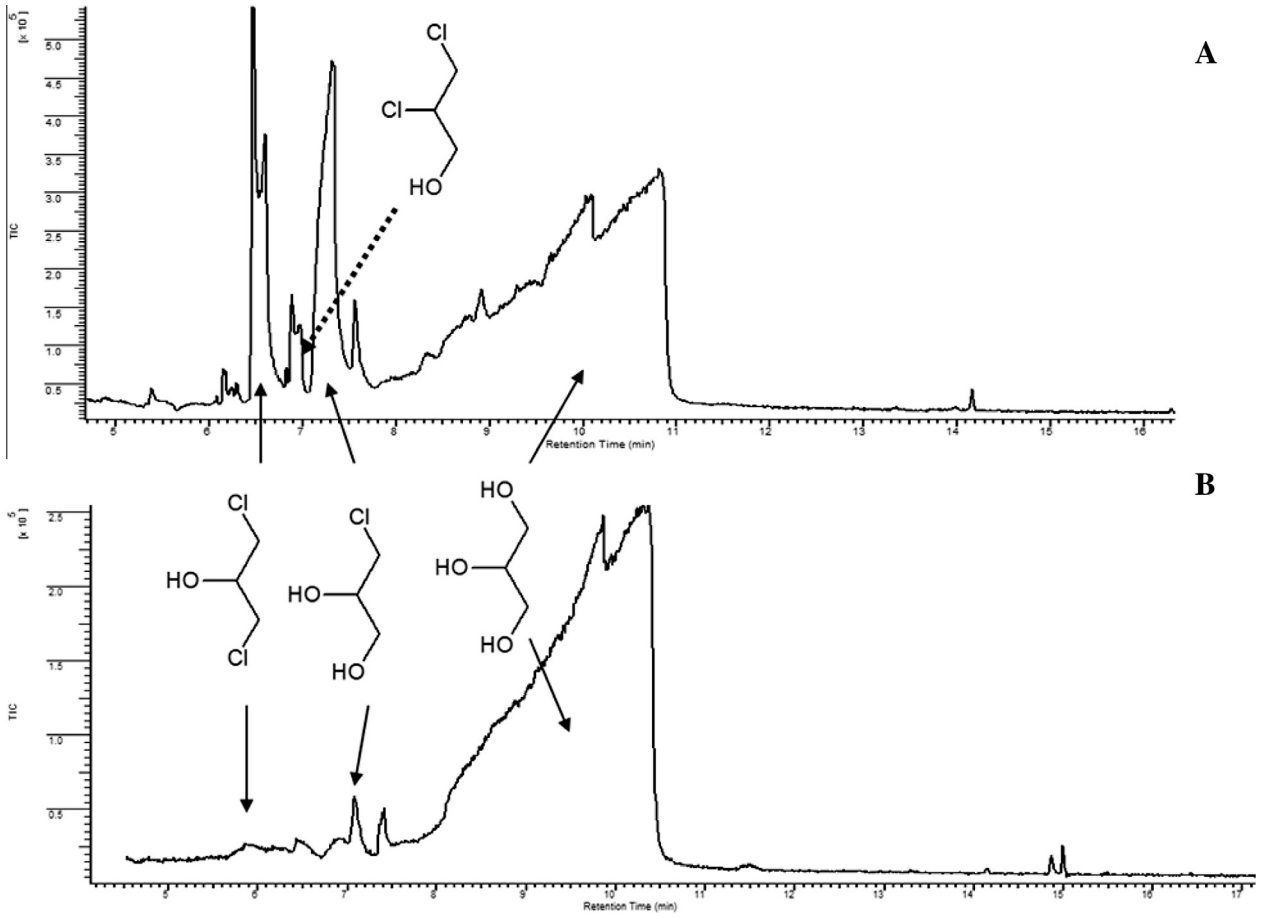


Fig. 2. Comparison of pyrolysis–GC/MS profiles of (A) glycerol/glycine hydrochloride and (B) reconstituted glycerol/glycine/NaCl mixtures.

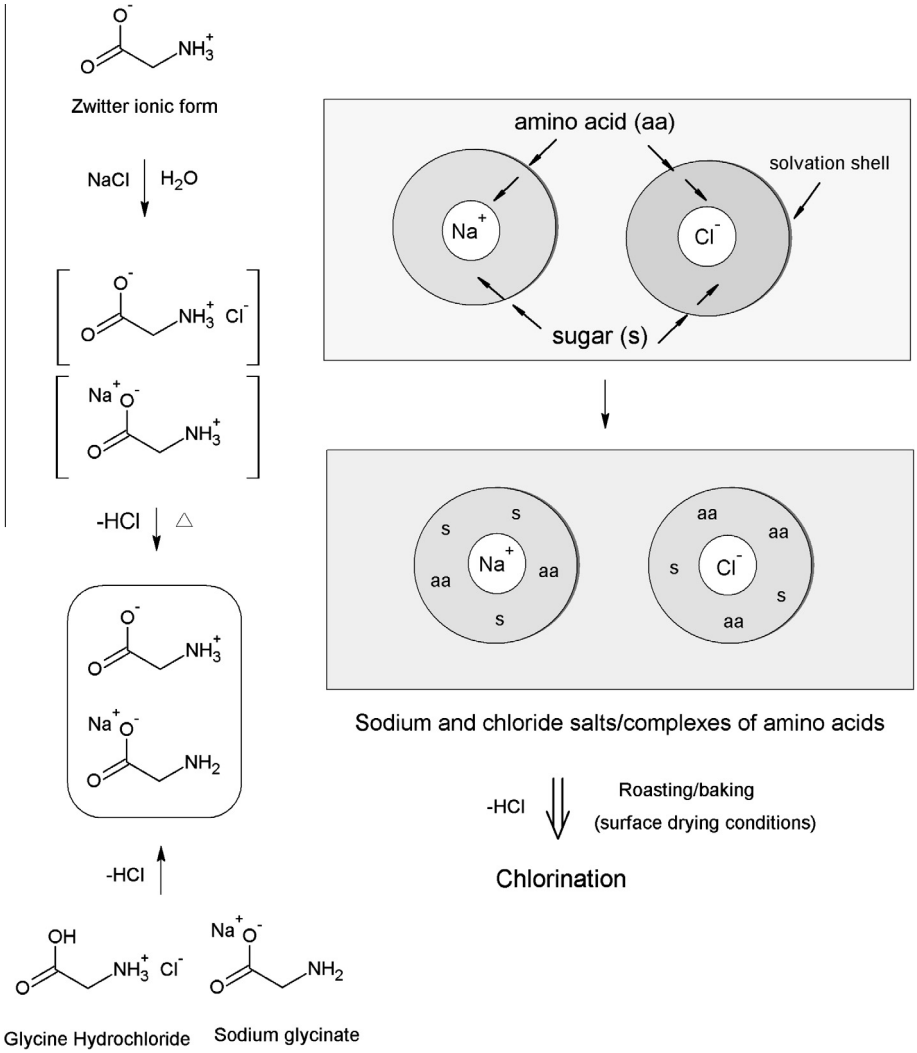


Fig. 3. Proposed hypothesis of activation of sodium chloride by amino acids upon dissociation of sodium and chloride ions in water and re-association with different ionic or polar sites in the mixture such as amino acids.

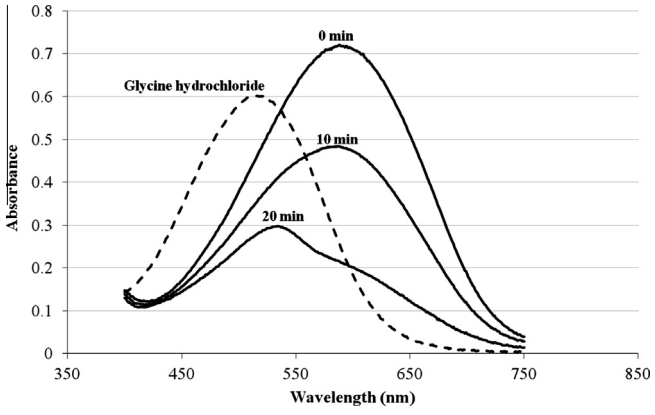


Fig. 4. Time-dependent (0–20 min) absorption spectra (400–700 nm) of concentrated NaCl/glycine solutions (4.8 M) at room temperature.

over a period of 20 min and are shown in Fig. 4. During this time a dramatic drop in the intensity of the peak at 600 nm with a simultaneous increase in intensity of a peak at 524 nm was observed. These observations are consistent with the chemical changes shown in Fig. 3 indicating the release of HCl into the reaction medium with subsequent lowering of pH, similar to the action of a solution of glycine hydrochloride.

3.2. Comparison of the chemical composition of residues of heated solutions of NaCl/glycine and glycine hydrochloride/sodium glycinate mixtures

It could be argued that chemically identical residues can be generated from heated mixtures of glycine hydrochloride/sodium glycinate and glycine/NaCl as shown in Fig. 3. Consequently, dissolution of a 2:1 M mixture of glycine/NaCl should generate a chemically equivalent residue to an equimolar mixture of free glycine/sodium glycinate upon heating and after complete release of HCl. The resulting basic character will depend upon the degree of HCl loss during the process (see Fig. 3). As shown above, highly concentrated solutions of the above model systems can behave similarly, altering the pH of the medium.

Glycine hydrochloride/sodium glycinate and free glycine/NaCl (2:1) mixtures were heated in an oven at 100 °C for an hour to completely release all the HCl expected to be formed and the dry residues were analysed by FTIR and their pH profiles were recorded. The colour test using the dye DCPIP indicated that both residues were not acidic, due to the absence of pink colour. In addition, the FTIR fingerprint of both residues showed more than 88%

correlation, indicating the similarity of their chemical composition. The above findings indicate a heated and dried solution of glycine/NaCl and a heated and dried aqueous solution of glycine hydrochloride/sodium glycinate can induce similar pH effects and generate similar chemical profiles after heating. In order to better observe the consequences of the chemical activation of NaCl and specifically chlorination, the subsequent experiments were performed using glycine hydrochloride instead of reconstituted NaCl/glycine mixture (after dissolving and heat drying).

3.3. Pyrolytic chlorination of glycerol, amino acids and Maillard reaction products using glycine hydrochloride

The ability of sodium chloride to be an effective chlorinating agent in the presence of an amino acid was first evaluated in its capacity to generate chloropropanols (CPs) from glycerol (Calta et al., 2004; Crews et al., 2001; Doležal et al., 2009; Hamlet et al., 2011; Reece, 2005). As indicated above, adding sodium chloride to glycine–glycerol mixture did not induce any chlorination; however, when the mixture was completely dissolved in water and re-analysed after a drying step, the model system generated not only 3-CP but also its dichlorinated derivatives (see Fig. 2). The intensities of the same CPs were significantly enhanced when sodium chloride–glycine mixture was replaced with equimolar amount of glycine hydrochloride (Fig. 2) indicating that for all practical purposes we can replace sodium chloride–glycine mixture with equimolar amount of glycine hydrochloride keeping in mind the differences in the intensities of the chlorinated peaks.

3.3.1. Chlorinated Maillard reaction products

To identify possible chlorination products that may form during the Maillard reaction in the presence of sodium chloride and amino acids, various model systems were evaluated using glycine hydrochloride instead of reconstituted sodium chloride/glycine mixtures to enhance the intensities of the peaks, facilitating their identification. The Maillard reaction plays a critical role in the generation of desirable aromas, colours and flavours during the thermal processes involving the surface drying of food products, e.g., baking and roasting. In most of these products sodium chloride is an essential component that may become activated, as described above, generating hydrochloride salts of amino acids or other ionic species during processing. These species in turn contain the potential to chlorinate a variety of Maillard reaction products and intermediates.

3.3.2. Chlorination of sugar degradation products

Pyrolysis of glucose and sucrose in the presence of glycine hydrochloride generated three chlorinated compounds, (chloromethyl)furan, (chloromethyl)furfural (CMF) and an unknown structure (see Table 2). The identity of CMF which is considered mutagenic (Surh & Tannenbaum, 1994) was confidently characterised by *in situ* generation of the standard (Table 1). Furthermore, good agreement was found between the mass spectrum of the synthesised CMF observed in soybean meal as reported by Velíšek, Ledahudcová, Pudil, Davídek, and Kubelka (1993), and the mass spectrum obtained in the current study. Reece (2005) also reported the formation of CMF in fresh protein hydrolysates. On the other hand, pyrolysis of glycidol in the presence of glycine hydrochloride generated four out of seven possible chloropropanols that were positively characterised using commercial standards (Table 1).

3.3.3. Chlorination of amino acids alone or in the presence of sugars

Chlorination of ten amino acids (see Table 1) was studied alone and in the presence of glucose and sucrose. No chlorinated species were detected in aspartic acid, arginine and threonine when analysed alone, while the remaining amino acids generated eight

Table 2
The mass spectra of chlorinated [a] compounds generated from different model systems.

Model systems	Mass spectrum[b]	Chlorine content	Retention time (min)
Proline	141 (1), 139 (8), 137(16), **114 (8)**, **112 (40)**, **110 (69)**, 102 (27), 77 (32), 75 (100), 41 (42), 39 (83), 38 (24), 37 (22), 28 (25)	2	13.81
Asparagine	**193 (34)**, **191 (100)**, 173 (32),163 (52), 151 (19), 147 (54), 135 (16), 133 (51), 119 (18)	1	14.86
All amino acids + glucose/sucrose	**132 (8)**, **130 (24)**, 95 (100), 67 (11), 65 (13), 52 (7), 51 (12), 50 (13), 43 (29), 41 (12), 39 (14)	1	15.30
Proline	**93 (31)**, **91 (100)**, 70 (18), 69 (33), 55 (55), 43 (34), 42 (18), 41 (72), 39 (45), 27 (46)	1	17.43
Threonine + glucose/sucrose	**124 (8)**, **122 (24)**, 86 (54), 85 (14), 58 (61), 41 (18), 39 (13), 30 (100), 29 (21), 28 (37), 27 (10)	1	17.58
Phenylalanine	**125 (100)**, **127 (35)**, 99 (9), 90 (7), 89 (30), 63 (17), 62 (8), 51 (9), 50 (12), 39 (13)	1	19.12
Glucose/sucrose	**163(3)**, **165(1)**, 99 (100), 97 (17), 71 (35), 69 (8), 53 (10), 43 (30), 41 (21), 39 (25), 29 (24), 27 (9)	1	22.28
Serine	**174 (20)**, **172 (68)**, 137 (21), 110 (100), 95 (77), 82 (27), 68 (21), 40 (20), 28 (23), 27 (32)	1	24.69
Tyrosine + glucose/sucrose	**158 (11)**, **156 (34)**, 108 (8), 107 (100), 91 (8), 79 (5), 77 (16), 65 (5), 39 (8), 27 (5)	1	24.69
Glutamic acid	**93 (32)**, **91 (100)**, 73 (27), 69 (53), 57 (52), 55 (51), 43 (59), 41 (77), 39 (29), 27 (33)	1	24.77
Phenylalanine + glucose/sucrose	**244 (6)**, **242 (21)**, 206 (22), 194 (17), 193 (100), 129 (13), 115 (34), 103 (15), 91 (20), 77 (16), 51 (12)	1	31.51
Phenylalanine + glucose/sucrose	**244 (7)**, **242 (25)**, 206 (20), 194 (19), 193 (100), 128 (18), 115 (45), 103 (14), 91 (19), 77 (18), 51 (14)	1	32.64

[a] Based on the natural isotope signature of chlorine atom.
[b] Bold ions represent chlorine signature.

chlorinated compounds (see Table 1 and 2). Most of the chlorinated compounds generated from the amino acids alone remain unidentified, except 2-(chloromethyl)benzene from phenylalanine, a recognised carcinogen (Henschler, 1994). The tentative identification of 2-(chloromethyl)benzene was further supported through *in situ* generation from known precursors (Table 1) confirming the mass spectrum and the retention time of tentatively characterised 2-(chloromethyl)benzene within a styrene model system. Thermal chlorination of styrene also provided evidence for the identity of an additional compound detected in the phenylalanine model system, characterising it as 2-(chloroethyl)benzene; furthermore, 2-(chloroethyl)benzene was generated in tyrosine models as well. While the identities of the remaining chlorinated amino acid degradation products remain unknown, their details are listed in Table 2. Model systems containing both saccharide and amino acid components resulted in the generation of additional chlorinated compounds listed in Table 2.

3.4. Other potential implications of hydrochloride salt formation from NaCl/amino acid mixtures

Although NaCl/amino acid mixtures are predicted to generate various chlorinated compounds as demonstrated above, not all the changes observed in the reaction profiles can be rationalised based on the formation of chlorinated species or their further reactions as suggested by Reece (2005). The released HCl not only can chlorinate the appropriate substrates but also can alter the acidity of the environment and influence the chemical pathways of the Maillard reaction and even catalyse hydrolytic reactions. In order to isolate the effect of induced acidity from chlorination, glycine hydrochloride was replaced with oxalic acid in selected model systems (see Table 1). Models pyrolysed in the presence of oxalic acid generated an almost identical pyrolysis profile to that of models studied in the presence of glycine hydrochloride, indicating that the induced acidity had the dominating effect over chlorination in generating new peaks. The magnitude of this effect could be attributed to the relatively high concentrations of glycine hydrochloride used in the experiments, which may not be as pronounced in hydrochloride salts generated from sodium chloride in food. Nevertheless, this allowed us to explore in general the role of HCl release from sodium chloride on the Maillard reaction. The acidic environment was observed to have two principal effects, which became evident when analysing different model systems. Maillard models incorporating glucose demonstrated enhancement of acid catalysed degradation pathways, while models containing sucrose generated products indicative of both acid catalysis as well as acid hydrolysis of sucrose, which has been observed recently in biscuit samples containing sodium chloride relative to control samples without added salt (Van der Fels-Klerx et al., 2014). In addition, the observed overall decrease (~70%) in pyrazines and increase in carbohydrate degradation products such as HMF by ~40% in the Maillard model systems suggests that acidification is responsible for a fundamental shift in the Maillard reaction pathways with the introduction of sodium chloride.

4. Conclusions

Various experiments performed in this study indicate that when sodium chloride is added to a matrix with sufficient moisture to dissociate the salt, the sodium and chloride ions will partially re-associate themselves with other oppositely charged species forming upon heating sodium and hydrochloride salts. Concentration or dehydration of this matrix may result in the formation of new chemical species that have the capacity to release hydrochloric acid, thereby increasing the acidity and the chlorinating potential of the Maillard reaction mixtures. Furthermore, the chemical effects of adding salt will depend on various factors, such as the composition of the mixtures and the temperature of the system under study in addition to time. In heated dry systems, for example, initially the hydrochloride salts of amino acids may increase the acidity through release of gaseous HCl and cause chlorination reactions until all is lost; the remaining dry matrix may now show increased alkalinity due to the presence of sodium salts of amino acids. On the other hand, in heated aqueous systems, the released HCl may dissociate into hydronium and chloride ions and may persist in the solution longer, mainly causing chlorination and hydrolytic reactions. Consequently, the role of salt during processing of food products subjected to heating may be viewed not only as altering its degree of saltiness but also its chemical composition, through altering Maillard reaction pathways and inducing chlorination reactions.

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