in a fluid such as in whipped cream where a protein film stabilizes them. The size distribution and the stability of these dispersed air bubbles play a crucial role in the sensory attributes, especially the texture, of these products.

14.3 CHEMICAL INTERACTIONS OF FOOD COMPONENTS

14.3.1 Introduction

The chemical interactions of food components under conditions of storage and processing comprise predominantly the Maillard reaction, caramelization of sugars, other pyrolytic changes, interactions of quinones with amines and amino acids, various oxidation processes, and reactions of proteins in alkaline conditions. The results of these interactions may be desirable, for example, browning of the crust of bread, in coffee roasting, or onion frying. In other cases, they may be detrimental for the food quality, for example, in stored condensed milk or dry vegetables. In many reactions flavor substances are produced, which may or may not be desirable, depending on the particular food. The nutritional value and safety of foods may decrease due to loss of valuable components or formation of some mutagenic and carcinogenic compounds. However, the gain in sensory quality is most often much higher than the small loss in biological value.

14.3.2 The Maillard Reaction

14.3.2.1 Nomenclature and Substrates

The Maillard reactions are sometimes called nonenzymic browning because the end products are brown colored melanoidins. Nonenzymic browning is also caused by caramelization of sugars, interactions of quinones with amines and amino acids, or interactions of oxidized lipids with protein. Nonenzymic browning is easily distinguished from enzymic browning, which is related to enzymic oxidation of food polyphenols.

The most important saccharides participating in the Maillard reactions are glucose and fructose, while in meat it may be ribose. Among disaccharides, lactose is an important browning precursor in dairy products as is maltose in cereal products, such as malt. Sucrose is easily cleaved into glucose and fructose, especially on heating. Therefore, it can participate in nonenzymic browning quite easily. Sugars bound as glycosides, for example, in glycoproteins, glycolipids, and in heteroglycosides are less reactive, but the aglycones may be released during heating to yield free reducing saccharides.

The other reaction partners are proteins, peptides, amino acids, and other amine compounds. The reactive group of proteins is mainly the ε-amino group of the lysine residue. The end amino groups of peptidic chains may also participate in the reaction, but their concentration in proteins is at least several times lower than that of lysine. The guanidyl group of arginine or the thiol group of cysteine can also participate in Maillard browning. In some food products, especially in cheeses and fish, biogenic amines are also precursors of brown products. Ammonium hydroxide and ammonium salts are reactive as well as amines.

Aldehydes and other carbonyls also participate in the browning reaction. They may originate from sugar derivatives, such as ascorbic acid, but they may also be produced from other precursors, predominantly oxidized lipids.

14.3.2.2 The Mechanism and Products of Reaction

The Maillard browning reaction proceeds in three stages:

1. Reaction of an amine with a reducing sugar with the formation of glycosyl amine, followed by the Amadori rearrangement (Figure 14.14).

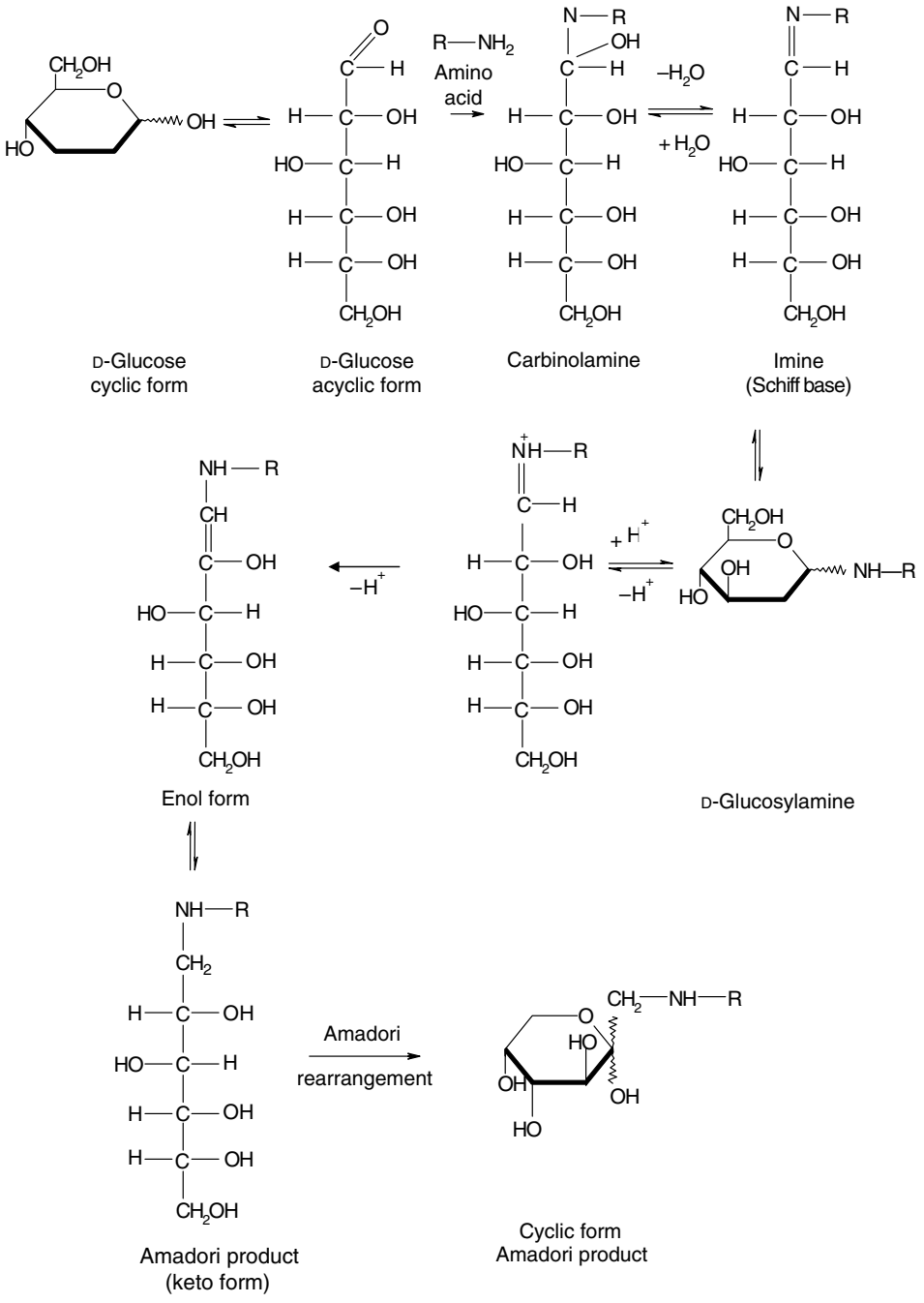

FIGURE 14.14 Formation of glucosylamine and Amadori rearrangement.

2. Dehydration of the intermediary products, fragmentation of the saccharidic moiety, and the Strecker degradation of the products (Figure 14.15).
3. Reactions of intermediary products resulting in the formation of heterocyclic flavor compounds, that is, high molecular weight brown pigments, which are responsible for the typical flavor of brown products (Figure 14.16).

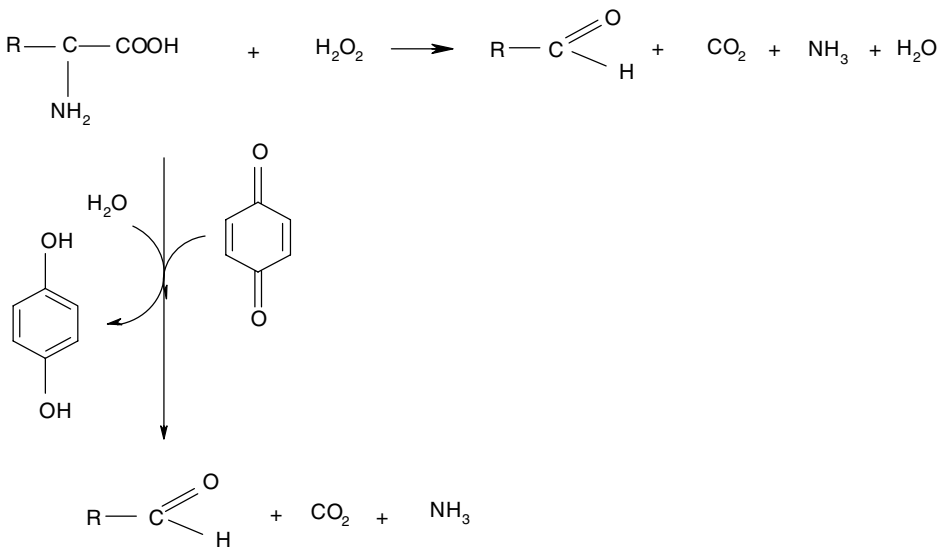

FIGURE 14.15 Strecker degradation of amino acids with oxidizing agents.

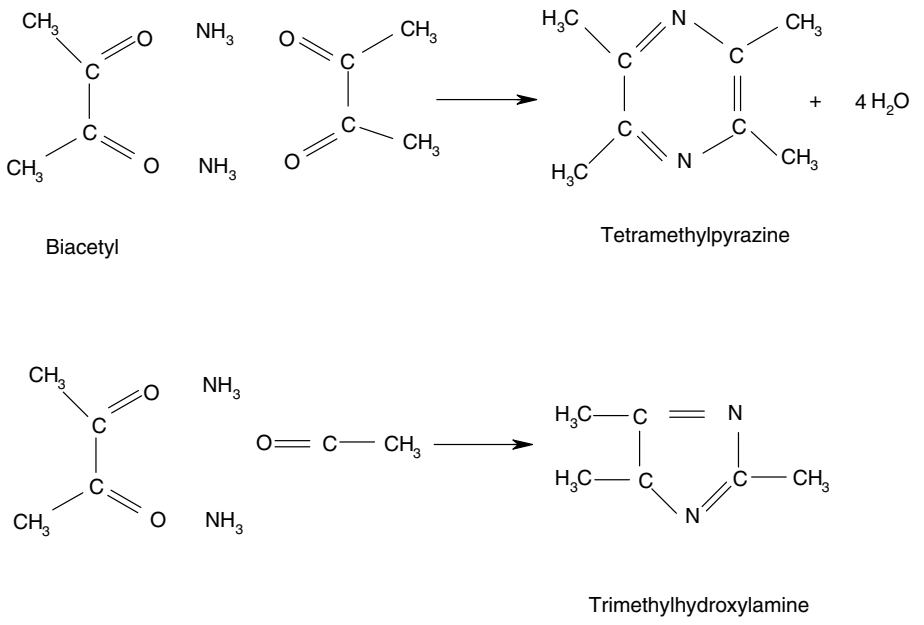

FIGURE 14.16 Formation of heterocyclic flavor compounds.

The Maillard reaction starts with the addition of a nonprotonized amine group to the electrophilic carbonyl carbon of a reducing sugar (Figure 14.14). The addition product, a monotropic carbonylamine or similar compound, is dehydrated with the formation of an imine or a Schiff base (or an azomethine). The addition rate increases with increasing electronic density of the nucleophilic amine. The inductive effect of the carbonyl group substituents and steric factors are also important.

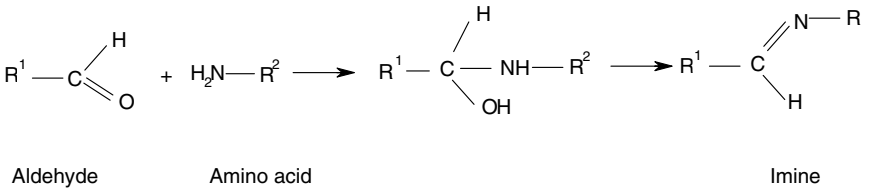

FIGURE 14.17 Reaction of carbonylic compounds with amine groups.

The reactivity of a carbonyl group decreases in the following series:

- Aldoses are more reactive with amino acids than ketoses.
- Trioses react with amino acids more rapidly than tetroses, tetroses more rapidly than pentoses, which are more reactive than hexoses and disaccharides.
- α-Dicarbonyl derivatives react with amino acids more easily than aldehydes, which are more reactive than ketones; reducing sugars are still less reactive, followed by oxo-acids.
- Acyclic form of sugars reacts more easily with amino acids than cyclic form of sugars.

The reactivity of amino compounds depends on their basicity: ammonium hydroxide and ammonium ions react with reducing sugars more easily than amines, whose reactivity decreases with their decreasing basicity.

Protonation of the carbonyl group increases its reactivity toward nucleophilic agents, while protonation of the amino group decreases the reactivity. Interactions of a carbonyl group with an amine group are shown in Figure 14.17. With decreasing pH, the concentration of protonated carbonyl group increases, but the concentration of nonprotonated amine group decreases. As a result, the reaction rate reaches a maximum in a slightly acidic medium in case of reaction with amines, while this occurs in a slightly basic medium in the case of reaction with amino acids.

The unstable Schiff's base is stabilized by consecutive reactions, for example, the reversible reaction between the carbonyl and the amine group. Glycosyl amines occur in aqueous solutions in the form of respective pyranoses or furanoses, similar to the original sugars. They also easily undergo mutarotation or are hydrolyzed into the original sugars and amine.

In the subsequent Amadori rearrangement the *N*-aldosyl amines yield ketosamines or 1-amino-1-deoxyketones, a step that is not reversible. *N*-ketosylamines are converted in the Heyns rearrangement into aldosamines or 2-amino-2-deoxyaldoses following a similar mechanism. Both reactions are acid catalyzed. Aldosamines occurring as furanoses are about ten times more reactive than the respective pyranoses. The reacting amino acid has the function of a catalyst at the same time, since its carboxyl group can donate the proton. Other carboxylic acids and phosphates also can catalyze the reaction.

Aldosyl amines derived from amino acids and other primary amines can react with another aldose molecule with the formation of dialdosyl amines. They are rearranged to diketosamines in a similar way as in the case of the Amadori rearrangement.

In the retroaldolization reaction of glycosylamines, very reactive dicarbon intermediary products are formed, for example, *N*-alkylimine of glycolaldehyde and D-erythrose. Alkylimines immediately dimerize into *N*, *N*′-dialkyldihydropyrazines, which are easily oxidized into pyrazinium salts. Imines are also hydrolyzed, forming glycol aldehyde, which is oxidized into glyoxal. Glyoxal is also produced by retroaldolization of hexos-2-uloses. Amino acids containing sulfur and aromatic groups are transformed into different heterocyclic compounds, for example, D-glucose reacts with cysteine forming 2-(D-*gluco*-1,2,3,4,5-pentahydroxypentyl)-thiazolidine-4-carboxylic acid.

All aminodeoxysugars (Figure 14.18) are strong reducing agents, more reactive than the original sugars. They mutarotate in aqueous solutions forming an equilibrium mixture of individual

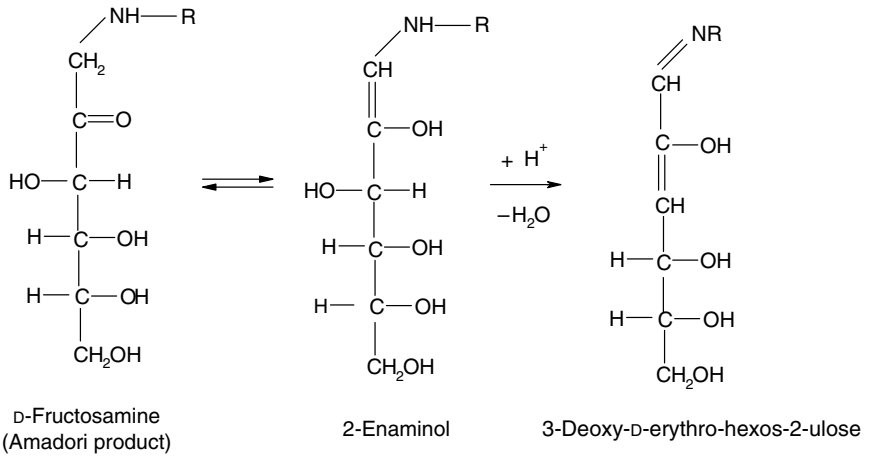

FIGURE 14.18 The 1,2-enolization of the Amadori product.

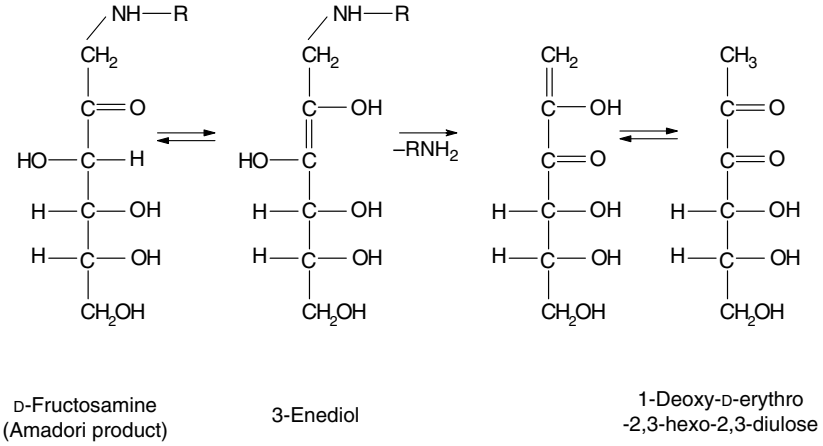

FIGURE 14.19 The 2,3-enolization of the Amadori product.

steric forms. Ketosamines (Amadori products) are relatively stable in the solid state or in neutral aqueous solutions. However, their stability is substantially lower than that of the original sugar, both in acidic and in alkaline media. The decomposition is more rapid if the compound exists in the furanose or acyclic form. The equilibrium mixtures always contain small amount of the acyclic form. Aldosamines (Heyns products) are decomposed similarly as ketosamines.

The decomposition of ketosamines begins with the 1,2-enolization. The amino analogue 1-en-1,2-diol or 1-en-1-amin-2-ol results from the degradation (Figure 14.18). The cleavage of the amino derivative 1-amino-2-deoxy-hexos-2-ulose results in the formation of 3-deoxy-D-erythro-hexo-2,3-diulose, which is further converted through dehydration into 3,4-dideoxy-D-*glycero*-hex-3-enos-2-ulose, 5-hydroxymethylfuran-2-carbaldehyde, and other compounds.

Another reaction is 2,3-enolization (Figure 14.19) with the formation of 2-ene-2,3-diol, which decomposes further to 1-deoxy-D-*erythro*-hexo-2,3-diulose. These products are similar to those formed during the degradation of sugars in the absence of amine derivatives, that is, during their caramelization, but amino acids and other amine derivatives catalyze the sugar degradation. The reaction proceeds readily at ambient temperature and in a slightly acidic medium (pH 4–7), common in foods. Although, mainly, 3- and 4-deoxy derivatives are formed in the absence of amino compounds, the

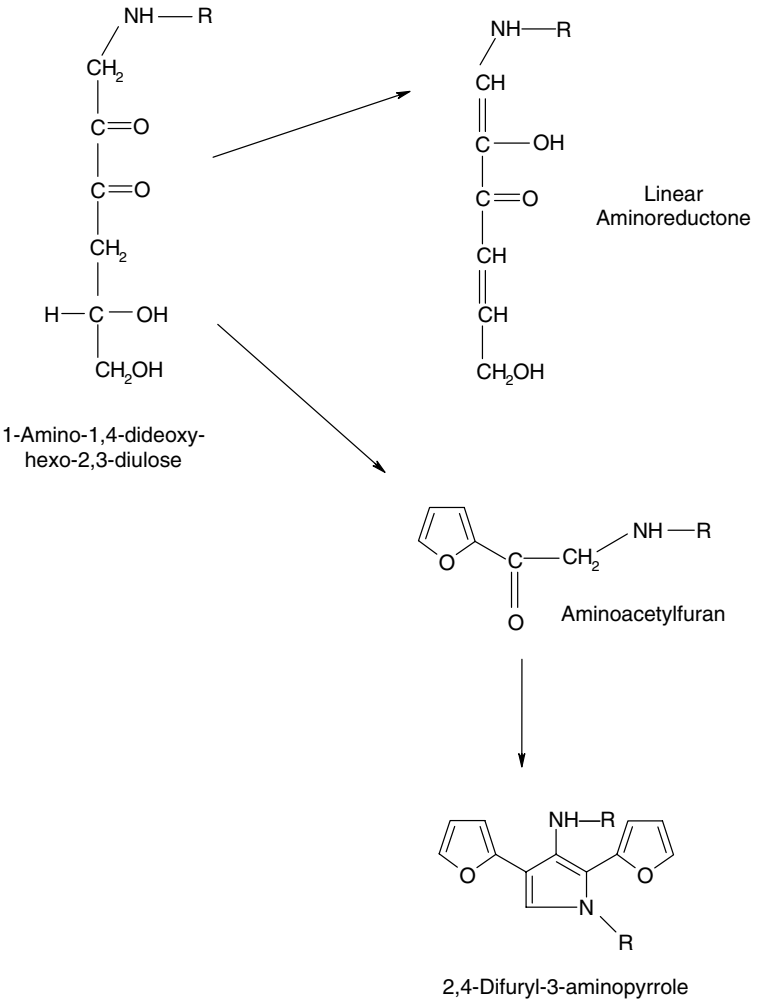

FIGURE 14.20 Degradation of 1-amino-1,4-dideoxy-2,3-diuloses into amino-reductones.

characteristic products in the presence of amino compounds are 1-deoxy derivatives. At higher temperatures, the 1,2- and 2,3-dehydration of ketosamines prevails.

In the presence of oxygen, ketosamines are decomposed into the respective glycos-2-hexosuloses. The reaction is catalyzed by transition heavy metals. The main products of the degradation of 3-deoxy-D-*erythro*-hexos-2-uloses are (*Z*)-3,4-dideoxy-D-*glycero*-hex-3-enos-2-ulose, the respective (*E*)-isomer, and 5-hydroxymethylfuran-2-carbaldehyde (Figure 14.19). Furan and pyrrole derivatives are formed if amine derivatives are present in excess (Figure 14.20). In the presence of amino acids, 1-carboxymethyl-substituted pyrrole-2-carbaldehydes are generated. Protein-bound lysine reacts with 3-deoxy-D-*erythro*-hexos-2-ulose forming pyrrole derivatives. Similarly, analogous compounds are produced by reactions with disaccharides.

Polyhydroxyalkyl-substituted pyrroles are formed by reaction of 3-deoxyhexos-2-uloses with ketosamines. In the presence of ammonia, the analogous pyrazines may form by dimerization of ketosamines. All polyhydroxyalkyl-substituted heterocyclic compounds can convert on heating into the respective alkyl-substituted derivatives.

Other Maillard reaction products, 1-deoxyglyco-2,3-diuloses, are also very reactive compounds, which have not been directly isolated from foods, but their degradation products, furanones, have

been. In the presence of cysteine, different thio derivatives are produced that are responsible for cooked or baked meat aroma.

Aminoreductones are produced by the degradation of 1-dideoxy-2,3-diuloses. They are easily transformed into 1-amino-1,4-dideoxy-hexo-2,3-diuloses, which are isomerized into the respective linear aminoreductones (Figure 14.20). The reaction is reversible, but shifted to the formation of aminoreductone. A parallel transformation product is aminoacetylfuran, which is dimerized into 2,4-difuryl-3-aminopyrrole. Another degradation product of 1-deoxyhexosones is a very reactive compound, diacetylformosin [2,4-dihydroxy-2,5-dimethyl-(2*H*)-furan-3-one], which reacts with primary amines to form substituted pyrrolidones and with secondary amines to form alicyclic aminoreductone. The analogous methylene reductonic acid is generated by reaction of deoxyosones with primary amines, and the analogous reductone acid is produced by interaction of amino acids with pentoses.

The Strecker degradation is a very important reaction of the sugar degradation products with amino acids. The reactive sugar derivatives are α-dicarbonylic compounds, such as glycos-2-ulose or glycos-2,3-diulose, and other simple compounds formed from sugar degradation, for example, glyoxal or methylglyoxal. Strecker degradation results in breakdown of amino acids to aldehydes, ammonia, and carbon dioxide. Each amino acid produces a specific aldehyde with a distinctive aroma (see Chapter 5) that further reacts with amine derivatives with the formation of flavor compounds typical for heated foods.

14.3.2.3 The Effect of Reaction Conditions

Temperature affects both the rate and the mechanism of the Maillard reaction. The activation energy varies between 10 and 160 kJ/mol. The water content has great influence on the activation energy. The browning rate increases with the increasing temperature reaching its maximum in the range of water activities of 0.3–0.7. At low water content, the reaction is slow; it increases with increasing concentration of water, but at much higher water contents, the concentration of reactants is low so that the reaction rate starts to decrease again. The rate of the Maillard reaction increases with increasing pH value, and attains its maximum in slightly alkaline medium. Browning is inhibited by sulfur dioxide and sulfites or sulfur-containing compounds, as sulfites react with aldehyde and keto group or sugars, decreasing their reactivity.

14.3.2.4 Nutritional Significance

The early products of the Maillard reaction involving the lysine residue can be nutritionally utilized in the human organism. Further changes, however, gradually make the amino acid unavailable. Generally lysine is affected mainly in the outer parts of conventionally heated products, exposed to high temperature during baking, grilling, or frying, whereas in the center of the bread loaf or cooked meat, the yield of the reaction products is negligible. However, in various liquid and powdered enteral proteinaceous food formulas produced commercially, the lysine availability may be decreased by up to 25% [11]. Such products are usually made of high-value proteins rich in lysine and the saccharide components may contain substantial amounts of reducing sugars. The same applies also to commercial infant formulas. In some products rich in proteins and reducing sugars, for example, condensed milk, the browning proceeds also at ambient temperature. Although the rate of reaction is much slower, the content of available lysine may drop by a few percent after several months of storage. The loss of nutritionally available lysine can be followed by determining the unchanged amino acid residue, or by assaying some early Maillard reaction products—furosine or N^{ε}-carboxymethyllysine.

It has been suggested that acrylamide may be formed in Maillard-type reactions between glucose and asparagine. In fried and roasted potatoes the concentration of acrylamide increases with the content of fructose and glucose in the raw material. Its content in the fried products can be significantly decreased by washing away the reducing sugars and asparagine from the surface of the cut potato

before frying [12]. Acrylamide interacts readily with the thiol group of cysteine, and, at a lower rate, with amino and hydroxyl groups of different food constituents—providing chemical strategies to curtail acrylamide accumulation.

14.4 REACTIONS DUE TO HEATING IN ALKALINE CONDITIONS

Other types of interactions occur in food systems due to alkaline treatment. Alkalis are applied in food processing for extraction and texturization of proteins from different sources, for example, oilseeds, grains, or bones from meat and poultry carcasses; inactivation of mycotoxins and protein inhibitors; removal of nucleic acids from single cell biomass; pealing of fruits and vegetables or during preparation of tortillas. The first step of the reactions in proteins heated in alkaline conditions is β-elimination in cysteine, serine, phosphoserine, and threonine residues due to attack of the hydroxide ion (see Chapter 5). The nucleophilic additions to the double bond of the dehydroalanine residue, formed as a result of β-elimination, lead to cross-linking of the polypeptide chains and to various unnatural compounds. In hydrolysates of proteins heated at high pH, among other amino acids, a mixture of L-lysino-L-alanine and L-lysino-D-alanine also appear, with probably a small proportion of DL and DD isomers, ornithinoalanine, lanthionine, and methyllanthionine. The products of reaction with ammonia and with phenylethylamine are diaminopropanoic acid and 3-(*N*-phenylethylamino)-alanine, respectively. Recombination of the carboanion with a proton leads to the formation of L and D amino acid enantiomers (see Chapter 5). Prolonged heating at alkaline conditions may decrease the nutritional value of proteins by loss of essential amino acids and racemization; the D-forms are absorbed at a lower rate than the L-forms. The D-enantiomers are not used for protein synthesis. Lysinoalanine chelates Cu^{2+}, Co^{2+}, and Zn^{2+}, thus inactivates metalloenzymes, and induces nephrocytomegaly in rats [13,14]. Also, other products generated due to heating of proteins at alkaline conditions, for example, diaminopropanoic acid and D-serine, are known to induce kidney damage.

A beneficial effect of heating at high pH is the release of nutritionally available niacin from grains. The traditional procedure of Hopi Indians of cooking mature corn grain with alkaline wood ashes hydrolyzed the ester linkages binding niacin to saccharides and turned the nutritionally unavailable polymer into free niacin [15].

14.5 WATER–PROTEIN AND PROTEIN–PROTEIN INTERACTIONS

14.5.1 Water in Proteinaceous Structures

The structural characteristics of proteins in moist food products are affected by their interactions with water via hydrogen bonding and hydrophobic interactions. Thus, protein–water interactions affect the stability of protein molecules and assemblies, for example, the casein micelles, and the functional properties of proteins in food raw materials and products.

Water constitutes about 60–85% of the mass of the tissues of beef, pork, poultry, fish, shellfish, and mollusks while the protein content is only about 12–22%. This large amount of water can be held in the meat against the action of gravity, centrifugal forces, or mechanical compression mainly due to compartmentation in the tissues and because of various interactions with protein molecules. This property of muscle foods, known as water holding capacity or water binding potential, can be characterized either by measuring the expressible liquid from a meat sample by pressing or centrifugation, or by adding water or an aqueous solution to the minced tissue and determining the quantity of water held by the sedimentable material in the centrifuge tube. Any treatment, additive, and biochemical process that favors loosening of the myofibrillar structure by enhancing mutual repulsion between