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Mechanism of Formation of Redox-Active Hydroxylated Benzenes and Pyrazine in ^{13}C-Labeled Glycine/D-Glucose Model Systems

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To extend the analytical capabilities of the pyrolysis−gas chromatograph−mass spectrometry system that has been successfully utilized in the past as an integrated reaction, separation, and identification system to study label incorporation patterns in Maillard reaction products, a novel methodology was developed to analyze the composition of nonvolatile residues of the initial reaction products. This was achieved through a postpyrolytic in-situ derivatization technique using trimethylsilyldiethylamine. Application of this technique to the investigation of the nonvolatile products formed during pyrolysis of glucose alone and in the presence of glycine has indicated the formation of several redox-active hydroxylated benzene derivatives such as 1,2,3-trihydroxybenzene (pyrogallol), 1,4-dihydroxybenzene (hydroquinone), 1,2-dihydroxybenzene (catechol), and 2,5-dihydroxypyrazine. Labeling studies have indicated that the intact glucose carbon backbone was involved in the construction of the benzene ring of the hydroxylated benzene derivatives and that dimerization of glycine alone can lead to the formation of 2,5-dihydroxypyrazine.

KEYWORDS: Maillard reaction; ^{13}C-labeling studies; silylation; mechanism of formation of phenolic compounds; dihydroxypyrazine; Py-GC-MS

INTRODUCTION

Although redox reactions play a crucial role in the generation of numerous Maillard reaction products (*1*), it is only recently (*2*) that electrochemical investigation of the reaction has been carried out. The electrochemical behavior of different model systems observed (drift toward more negative voltages over time) was consistent with the formation of reductones over time. Recently, the role of reductones in the Maillard reaction was elaborated by Yaylayan et al. (*3*). They concluded that the net outcome of the Maillard reaction in terms of color and aroma generation depends on the formation and balance among four key precursor moieties constituting a redox cycle: α-dicarbonyl, α-hydroxycarbonyl, α-aminocarbonyl, and 1-amino acid-2-carbonyl (*3*, *4*). This balance can be manipulated or disrupted through initiation of redox reactions that are affected by the amount of dissolved oxygen and by the amount and timing of the release of reducing species produced by the reaction, reductones, disproportionation and dehydration reactions, and concentration of metal ions. In principle, each α-dicarbonyl compound formed during the Maillard reaction (such as glyoxal, pyruvaldehyde, 1- and 3-deoxyglucosone, etc.) can generate its own redox cycle. In addition, measured redox potentials of different redox model systems progressively became more negative and the color generated upon heating intensified as the number of carbon atoms decreased in the moieties, indicating a correlation between more negative potentials and color-generating abilities. The significance of the proposed redox cycles lies in the fact that it allows assessment of color and aroma generation abilities of different Maillard precursors. In fact, the formation of color in many model and food systems (beer, cocoa, and coffee) has been found to correlate with more negative oxidation−reduction potentials (ORP) (*5*). Conversely, color originating from Maillard reaction mixtures can be decreased by the addition of oxidizing agents (*6*). The identity of redox-active structures in Maillard model systems so far has been limited to the well-established reductone moieties, although polyhydroxy aromatic compounds such as 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol), 1,4-dihydroxybenzene (hydroquinone), and 1,2,3-trihydroxybenzene (pyrogallol) are also redox-active compounds and have been identified in model and Maillard related systems such as humic substances (*7*) and coffee (*8*) and in sugar or sugar−amino acid mixtures (*9*). During the cocoa bean drying process, the chocolate brown color produced is primarily due to the oxidative fermentation of polyphenols (*10*). Phenolics released and produced during the malting process are assumed to be primarily responsible for the reductive ORP of beer (*11*), which can be correlated to color formation. Variously substituted phenols have also been identified in commercial smoke flavorings (*12*) made from different wood sources. Reese et al. (*13*) also demonstrated that 2,3-butanedione/serine reaction mixtures could produce phenols

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Table 1. Mass Spectrometric Data[a]

pyrazine, 2,5-bis-*O*-trimethylsilyl-
241 (100), 256 (26), 242 (20), 255 (5), 73 (62), 243 (8), 182 (3), 45 (24), 257 (6), 43 (11)
241 (100), 256 (31), 242 (22), 255 (17), 73 (16), 243 (8), 182 (8), 45 (8), 257 (6), 43 (6)
silane, [1,4-phenylenebis(oxy)]bis[trimethyl-
239 (100), 254 (74), 73 (29), 241 (8), 255 (14), 223 (4), 45 (7), 43 (2), 112 (18), 256 (39)
239 (100), 254 (97), 73 (23), 241 (17), 255 (14), 223 (12), 45 (12), 43 (10), 112 (7), 256 (7)
silane, [1,2,3-benzenetriyltris(oxy)]tris[trimethyl-
239 (100), 342 (54), 73 (98), 240 (22), 343 (19), 327 (10), 211 (6), 45 (19), 344 (8), 241 (9)
239 (100), 342 (57), 73 (25), 240 (20), 343 (18), 327 (17), 211 (12), 45 (9), 344 (8), 241 (8)
phenol, 2-[(trimethylsilyl)oxy]-
151 (34), **182 (100),** 166 (46), 167 (44), 75 (21), 73 (42), 45 (10), 91 (18), 136 (16), 183 (25)
151 (99)**, 182 (100),** 166 (97), 167 (78), 75 (63), 73 (39), 45 (24), 91 (19), 136 (18), 183 (18)

[a] The first row of values for each compound is the standard.

and various volatile benzene compounds. Monosaccharides, exposed to alkaline conditions, have also been found to form a variety of phenolics (*14*). Their formation could have a significant effect on the redox potential of the system and hence influence the degree of browning. To elucidate the molecular mechanism of formation of polyhydroxy benzenes and other related redox systems during Maillard reaction, variously labeled D-glucose and glycine model systems were analyzed using pyrolysis−gas chromatography−mass spectrometry (Py-GC-MS) with the application of a postpyrolytic derivatization technique.

MATERIALS AND METHODS

All reagents and chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI). The labeled sugars [1-^{13}C]glucose (99%), [2-^{13}C]-glucose (99%), [3-^{13}C]glucose (99%), [4-^{13}C]glucose (99%), [5-^{13}C]-glucose (99%), [6-^{13}C]glucose (99%), [U6-^{13}C]glucose (99%), [1-^{13}C]-glycine (99%), [2-^{13}C]glycine (99%), and [^{15}N]glycine (98%) were purchased from Cambridge Isotope Laboratories (Andover, MA).

Py-GC-MS Analysis. 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 used for Py-GC-MS analysis. In all experiments, glucose/glycine model mixtures (0.5 mg, equimolar), with or without silica gel, were introduced inside the quartz tube (0.3 mm thickness), plugged with quartz wool, and inserted into the coil probe. Prior to pyrolysis, argon gas was directed at the entrance of the pyroprobe interface to prevent the introduction of air into the pyroprobe interface. The pyroprobe interface temperature was set at 250 °C. Model systems were pyrolyzed in two stages; the initial pyrolysis was performed to release the volatiles and generate a nonvolatile residue to be subsequently derivatized and desorbed through a second pyrolysis step. The initial pyrolysis was performed at 250 °C with a total heating time of 20 s and repeated three consecutive times to make sure all of the volatile products were released. Samples were then left in the interface for a total of 2 min, and then the probe was removed and immediately cooled with argon gas to prevent oxidative browning of the samples. After cooling, 1 μL of derivatization agent trimethylsilyldiethylamine (TMSDEA) was introduced inside the quartz tube with a syringe to derivatize the nonvolatile residue. After 5 min, the samples were introduced into the interface under a steady stream of argon. The samples were desorbed at 100 °C and ramped at 10 °C/s to 175 °C for 20 s and left in the interface for a total of 2 min. The initial temperature of the column was set at −5 °C for 12 min and then increased to 50 °C at a rate of 50 °C min^{-1}; immediately, the temperature was further increased to 250 °C at a rate of 8 °C min^{-1} and kept at 250 °C for 5 min. A constant flow of 1.5 mL min^{-1} was used during analysis. The capillary direct MS interface temperature was 250 °C, and the ion source temperature was 180 °C. The ionization voltage was 70 eV, and the electron multiplier was set at 2047 V. The mass range analyzed was 29−300 amu. The column was a fused silica DB-5 MS column (50 m length 0.2 mm i.d., 0.33 μm film thickness; J&W Scientific). The identity and purity of the chromatographic peaks were determined using NIST AMDIS version 2.1 software (see **Table 1**) and through comparison of retention times of commercial standards (as in the case of hydroxylated benzene derivatives). The reported percent label incorporation values (corrected for natural abundance and for percent enrichment) are the average of duplicate analyses and are rounded off to the nearest multiple of 5%.

Color Measurements. *Sample Preparation.* A stock mixture containing pyrogallol, hydroquinone, and resorcinol (0.1 mM in each) was prepared and diluted with neutral silica (0.1 g) and was termed mixture A. In addition, glycine, D-glucose, and an equimolar mixture of D-glucose and glycine samples were prepared by dilution with 14% w/w neutral silica. Each of the three samples was mixed with 3.33% w/w of stock mixture A, resulting in three phenolic mixtures consisting of 0.66 mol of each phenol per mole of the reactants. Triplicates of all six model systems were pyrolyzed as indicated above at 170 °C under air for 2 min.

Color Measurements. After pyrolysis, the tubes containing the heated model systems were placed in separate vials and filled with distilled water (1.0 mL). The vials were closed and vortexed, making sure all of the water-soluble materials were extracted. The content of each vial was transferred into a cuvette and allowed to rest for ∼10 min, so that non-water-soluble materials could settle to the bottom. The visible spectra (400−700 nm) of the clear solutions were used to calculate Tristimulus color coordinates using Galactic "Color" add-on application software.

RESULTS AND DISCUSSION

To extend the analytical capabilities of the Py-GC-MS system that has been successfully utilized in the past as an integrated reaction, separation, and identification system to study label incorporation patterns in Maillard reaction products (*15*), novel methodologies were developed to analyze the composition of nonvolatile residues of the initial reaction products and to perform the reactions under air or in the presence of moisture (*3*). The analysis of nonvolatiles was achieved through a postpyrolytic in-situ derivatization technique as described under Materials and Methods. Application of this technique to the investigation of the nonvolatile products formed during the pyrolysis of glucose alone and in the presence of glycine has indicated the formation of several hydroxylated benzene derivatives such as 1,2,3-trihydroxybenzene (pyrogallol), 1,4-dihydroxybenzene (hydroquinone), 1,2-dihydroxybenzene (catechol), and 2,5-dihydroxypyrazine among others. Identification of these redox-active moieties, albeit in relatively low concentrations, may expand the concept of reductones formed during the Maillard reaction to also include phenolic compounds.

Postpyrolytic Derivatization of Nonvolatiles Produced during Py-GC-MS Analysis. Nonvolatiles produced from pyrolysis of glucose/glycine model systems were derivatized with three silylating agents having different silyl donor strengths.

N,O-Bis(trimethylsilyl)acetamide (BSA), trimethylsilyldiethylamine (TMSDEA), and hexamethyldisiazane (HMDS) were chosen so that a range of reactivities (*16*) could be tested:

TMSI > BSTFA > **BSA** > MSTFA > TMSDMA > **TMSDEA** > MSA > TMCS (with base catalyst) > **HMDS**

TMSDEA was found to be the most efficient because its utilization required a shorter sample preparation time and produced fewer artifacts originating from the reagent. Several factors were found to enhance the abundance of the desired peaks while minimizing the artifact formation, such as maintaining a reductive environment during cooling of the sample after pyrolysis and just before derivatization. Samples exhibited instantaneous color formation when exposed to air during the withdrawal of the pyrolysis probe from the interface and its exposure to air. These oxidative changes significantly darkened the residue, possibly changing its composition. Therefore, prior to derivatization, oxidative browning was prevented by maintaining an inert environment during heating or cooling of the Maillard model systems. This was achieved by flushing the inlet of the pyrolysis interface with argon when the sample was either inserted or removed. Once removed from the interface after initial pyrolysis, argon gas was also utilized to cool the sample. Maintaining an inert environment during pyrolysis of nonvolatiles also limited the formation of artifacts generated from interactions between atmospheric oxygen and the silylation agents (*16*). Optimization of the sample preparation techniques significantly affected the derivatization of nonvolatiles and limited the production of artifacts. Postpyrolytic residues generated from the initial stage of pyrolysis were derivatized at a lower temperature; this prevented any residual volatiles in the matrix or degradation products from being silylated. The optimal amounts of different silylating reagents applied were varied, but for TMSDEA, ~1.0 μL produced the best results. The period between the application of the reagent to the residue and pyrolysis was also found to be important. Samples pyrolyzed immediately after application of silylating agent produced too many products originating solely from the reagent, whereas samples pyrolyzed after 30 min seemed to have lost many of the derivatized products by volatilization. A 5 min pause between derivatization and desorption through pyrolysis was found to be the optimal time because it enabled some excess reagent to volatilize and provided enough reaction time for derivatization.

Proposed Mechanism of Formation of Hydroxylated Benzenes. Color formation from the oxidation of phenolic compounds is widely documented in food products (*11*), but it has not been investigated in Maillard model systems. The identification of hydroxyphenols in glucose and glucose/glycine model systems is consistent with the phenomenon of oxidative browning known to occur also in Maillard model systems. Hydroxylated phenols may constitute an important color precursor system that can be activated when oxidized. Furthermore, they could partly be responsible for the lowering of redox potential associated with the generation of color. As shown in **Table 2**, browning of the glucose/glycine model system increased significantly in the presence of phenolic compounds, as measured by their Tristimulus $\times$ coordinate values.

Label incorporation studies have indicated that 1,2,3-trihydroxybenzene (pyrogallol), 1,4-dihydroxybenzene (hydroquinone), and 1,2-dihydroxybenzene (catechol) were all formed through the incorporation of only glucose carbon atoms (see **Table 3**). Furthermore, the data also indicated that the intact carbon chain of the glucose backbone formed the six-membered ring of the benzene moiety, as evidenced by the absence of label scrambling and lack of multiply incorporated carbon atoms. Consequently, when glucose was pyrolyzed alone, it also generated the same hydroxylated benzene derivatives with identical label incorporation patterns. However, it seems likely that glycine could have played a possible role as acid/base catalyst because, in its absence, the formation of these compounds was significantly diminished. The conclusions derived from the experimental data imply a process of ring closure involving carbon atoms 1 and 6 of glucose as shown in **Figure 1**. According to this figure, the open ring form of glucose can undergo dehydration initiated from carbon atoms 5 and 6 to produce a 1,5-dicarbonyl intermediate (**1**) that can undergo a facile intramolecular aldol addition reaction followed by condensation. The aldol addition product (**2**) after a reduction step can undergo multiple dehydration reactions to produce dihydroxybenzenes; similarly, the aldol condensation product (**3**) can also undergo a dehydration step to produce trihydroxybenzene.

Proposed Mechanism of Formation of 2,5-Dihydroxypyrazine. The 2,5-dihydroxypyrazine has not been identified in food or in model systems. On the basis of the label incorporation pattern shown in **Table 4**, it is clear that only glycine carbon atoms are involved in the formation of 2,3-dihydroxypyrazine. Furthermore, **Table 4** shows that, as expected, it also incorporates two nitrogen atoms from glycine. Model systems containing no glucose generated a third of the amount of this hydroxypyrazine, suggesting a possible catalytic role as oxidant for glucose. It is also worth mentioning that unlike most nonvolatiles identified, this particular pyrazine could be generated only when the model systems were mixed with

Table 2. Effect of Addition of Phenolic Compounds on Color of Heated Model Systems

model	average Tristimulus values		
	X	*Y*	*Z*
glucose	0.068 ± 0.007	0.066	0.034
glucose + phenolic mix[a]	0.097 ± 0.009	0.089	0.042
glycine	0.043 ± 0.006	0.040	0.020
glycine + phenolic mix	0.131 ± 0.007	0.130	0.064
glucose + glycine	0.412 ± 0.027	0.450	0.512
glycine + glucose + phenolic mix	0.633 ± 0.019	0.657	0.570

[a] A mixture of pyrogallol, resorcinol, hydroquinone, and catechol (see Materials and Methods).

Table 3. Percent Label Incorporation[a] in Silylated 1,2,3-Trihydroxybenzene (Pyrogallol), 1,4-Dihydroxybenzene (Hydroquinone), and 1,2-Dihydroxybenzene (Catechol) Formed in Glucose/Glycine Model System

compound	M	M + 1	M + 2	M + 3	M + 4	M + 5	M + 6
D-glucose-U-$^{13}C_6$/glycine	0	0	0	0	0	0	100
D-glucose-6-^{13}C/glycine	0	100	0	0	0	0	0
D-glucose-5-^{13}C/glycine	0	100	0	0	0	0	0
D-glucose-4-^{13}C/glycine	0	100	0	0	0	0	0
D-glucose-3-^{13}C/glycine	0	100	0	0	0	0	0
D-glucose-2-^{13}C/glycine	0	100	0	0	0	0	0
D-glucose-1-^{13}C/glycine	0	100	0	0	0	0	0
D-glucose/glycine-1-^{13}C	100	0	0	0	0	0	0
D-glucose/glycine-2-^{13}C	100	0	0	0	0	0	0
D-glucose/glycine-^{14}N	100	0	0	0	0	0	0

[a] A similar label incorporation pattern was observed in the absence of glycine.

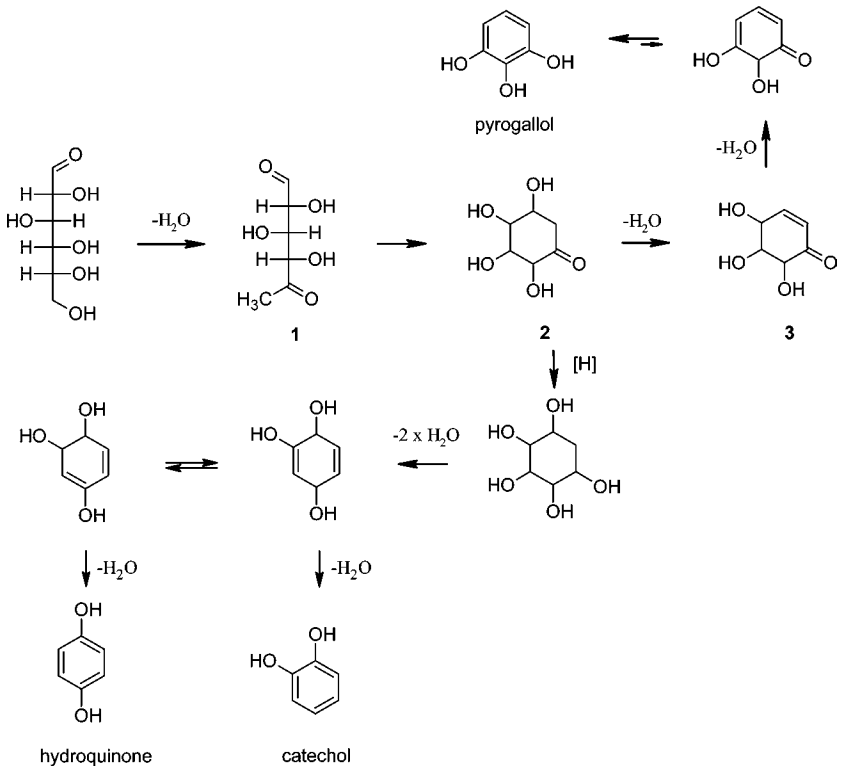

Figure 1. Proposed mechanism of formation of hydroxylated benzene derivatives.

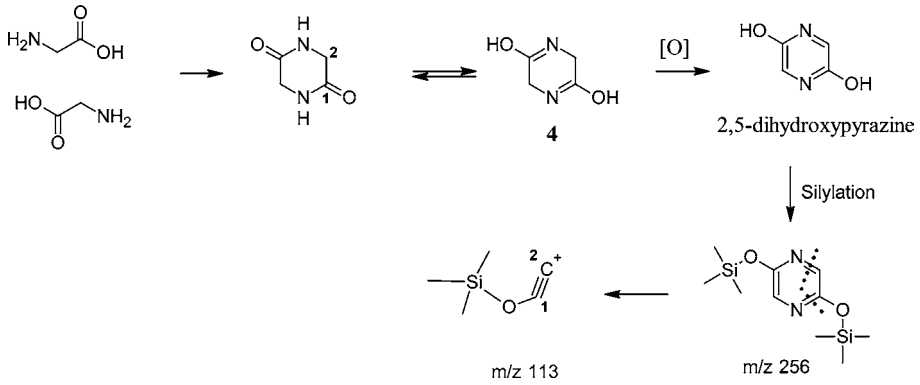

Figure 2. Proposed mechanism of formation of 2,5-dihydroxypyrazine. Numbers represent original glycine carbon atom locations.

Table 4. Percent Label Incorporation in Silylated 2,5-Dihydroxypyrazine Formed in Glucose/Glycine Model System

compound	M	M + 1	M + 2	M + 3	M + 4	M + 5	M + 6
D-glucose-U-$^{13}C_6$/glycine	0	0	0	0	0	0	0
D-glucose-6-^{13}C/glycine	0	0	0	0	0	0	0
D-glucose-5-^{13}C/glycine	0	0	0	0	0	0	0
D-glucose-4-^{13}C/glycine	0	0	0	0	0	0	0
D-glucose-3-^{13}C/glycine	0	0	0	0	0	0	0
D-glucose-2-^{13}C/glycine	0	0	0	0	0	0	0
D-glucose-1-^{13}C/glycine	0	0	0	0	0	0	0
D-glucose/glycine-1-^{13}C	0	100	0	0	0	0	
D-glucose/glycine-2-^{13}C	0	0	100	0	0	0	0
D-glucose/glycine-^{14}N	0	0	100	0	0	0	0

neutral silica during pyrolysis. This fact can be attributed to the ease of dimerization of glycine on silica gel (*17*). The proposed mechanism of formation of 2,5-dihydroxypyrazine is shown in **Figure 2**. The piperazine-2,5-dione (**4**), formed after dimerization of glycine, can undergo oxidation to from 2,5-dihydroxypyrazine. Thermally induced dimerization of amino acids to form piperazine-2,5-diones (**4**) has been reported for glycine, alanine, and proline (*18*). Furthermore, addition of commercially available cyclic glycine anhydride (intermediate **4** in **Figure 2**) to the glucose/glycine model system increased the intensity of the 2,5-dihydroxypyrazine peak by 3-fold under identical conditions, supporting the proposed mechanism. In addition, glycine anhydride alone also generated 2,5-dihydroxypyrazine under oxidative conditions. Labeling studies have also indicated that the fragment at *m*/*z* 113 (see **Figure 2**) incorporates only carbon atoms 1 and 2 of glycine, providing further evidence for the proposed structure.

The formation of phenolic intermediates during the Maillard reaction can have a significant effect on the redox potential of the system, through their participation in electrochemical processes and through catalysis or inhibition of redox active reactions. Benzoquinone, for example, has been shown to inhibit by 80% the formation of pyrazines during the Maillard reaction while accelerating the generation of 2,3-butanedione by 15% (*19*). Furthermore, phenolic compounds may also contribute to the overall color development during the Maillard reaction as demonstrated (see **Table 2**), bridging the gap between enzymatic and nonenzymatic browning reactions.

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