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Model Studies on the Oxygen-Induced Formation of Benzaldehyde from Phenylacetaldehyde Using Pyrolysis GC-MS and FTIR

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Benzaldehyde, a potent aroma chemical of bitter almond, can also be formed thermally from phenylalanine and may contribute to the formation of off-aroma. To identify the precursors involved in its generation during Maillard reaction, various model systems containing phenylalanine, phenylpyruvic acid, phenethylamine, or phenylacetaldehyde were studied in the presence and absence of moisture using oxidative and nonoxidative Py-GC-MS. Analysis of the data indicated that phenylacetaldehyde, the Strecker aldehyde of phenylalanine, is the most effective precursor and that both air and water significantly enhanced the rate of benzaldehyde formation from phenylacetaldehyde. Phenylpyruvic acid was the most efficient precursor under nonoxidative conditions. Phenethylamine, on the other hand, needed the presence of a carbonyl compound to generate benzaldehyde only under oxidative conditions. On the basis of the results obtained, a free radical initiated oxidative cleavage of the carbon−carbon double bond of the enolized phenylacetaldehyde was proposed as a possible major mechanism for benzaldehyde formation, and supporting evidence was provided through monitoring of the evolution of the benzaldehyde band from heated phenylacetaldehyde in the presence and absence of 1,1′-azobis(cyclohexanecarbonitrile) on the ATR crystal of an FTIR spectrophotometer. In the presence of the free radical initiator, the enol band of the phenylacetaldehyde centered at 1684 cm^{-1} formed and increased over time, and after 18 min of heating time the benzaldehyde band centered at 1697 cm^{-1} formed and increased at the expense of the enol band of phenylacetaldehyde, indicating a precursor product relationship.

KEYWORDS: Benzaldehyde; phenethylamine; phenylacetaldehyde; phenylpyruvic acid; phenylalanine; oxidation of phenylacetaldehyde; FTIR analysis; oxidative pyrolysis

INTRODUCTION

Benzaldehyde is produced naturally in different fruits such as bitter almond, cherry, apricot, and peaches through the action of β-glucosidases on cyanogenic glucosides followed by hydroxynitrile lyase (*1*). Enzymatic transformation of phenylalanine into benzaldehyde using cultures of microorganisms, molds, and enzyme extracts are also reported. Porter and Bright (*2*) used L-amino acid oxidase in the presence of horseradish peroxidase as an in vitro bienzymatic system to generate benzaldehyde from L-phenylalanine. Okrasa et al. (*3*) used D-amino acid oxidase from *Trigonopsis variabilis* and peroxidase from *Coprinus cinereus* to convert phenylalanine into benzaldehyde and proposed a mechanism starting from phenylalanine via the formation of phenylpyruvic acid and phenylacetaldehyde. Benzaldehyde has also been detected in numerous phenylalanine-containing model systems, where it can be produced thermally (*4*−*6*). Due to its strong sensory properties, its generation under Maillard reaction conditions in food products may impart off-flavor notes (*7*), especially in combination with phenylacetaldehyde, the Strecker aldehyde of phenylalanine. Recently, phenylacetaldehyde has been shown to be one of the off-aroma notes generated in aged beer (*8*). On the other hand, Brinkman et al. (*9*) identified benzaldehyde in the headspace of beef broth as one of the volatiles contributing to the characteristic aroma of beef. Severin and Braütigam (*4*) reported the formation of benzaldehyde through heating of phenylalanine, *N*-acetylphenylethylamine, or *N*-glycylphenylalanine alone or with triglycerides between 190 and 240 °C in the presence of air. The yield varied between 0.1 and 3.1%. Granvogl et al. (*5*) observed the formation of benzaldehyde from a heated mixture of phenethylamine and pyruvaldehyde and proposed a multistep mechanism based on imine isomerization, oxidation, and water addition steps. In the same study the authors made an interesting observation for the simultaneous generation of Strecker aldehyde and Strecker amine (decarboxylated amino acid) under Strecker reaction conditions. Furthermore, Zamora et al. (*6*) detected benzaldehyde in a model system heated at 60 °C containing phenylalanine and 4,5-epoxy-2-alkenal. They

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Table 1. Occurrence[a] of Benzaldehyde and Its Precursors in Different Model Systems

model system	phenylacetaldehyde	phenethylamine	benzaldehyde	benzaldehyde-imine adduct[b]
phenylalanine, 200 °C	0	0	0	+
phenylalanine, 200 °C, air	0	0	++	+
phenylalanine, 250 °C, He	0	+++	0	+
phenylalanine, 250 °C, air	0	++++	0	++
phenylacetaldehyde, 175 °C	+++	0	+	0
phenylacetaldehyde, 175 °C, water	+++	0	+	0
phenylacetaldehyde, 175 °C, air	+++	0	++	0
phenylacetaldehyde, 175 °C, air and water	+++	0	+++	0
phenylacetaldehyde, 250 °C, He	+++	0	++	+
phenylacetaldehyde, 250 °C, air	+++	0	+++	+
phenylacetaldehyde, 250 °C, air and water	+++	0	+++	+
glycolaldehyde/phenylalanine (1:1), 175 °C	+++	0	+	0
glycolaldehyde/phenylalanine (1:1), 250 °C	0	++++	0	+
glycolaldehyde/phenylalanine (2:1) 175 °C	+++	0	+	0
glycolaldehyde/phenylalanine (2:1), 250 °C	+++	0	+	0
glycolaldehyde/phenylacetaldehyde, 175 °C	+++	0	+	0
glycolaldehyde/phenylacetaldehyde, 175 °C, air and water	+++	0	+++	0
glycolaldehyde/phenylacetaldehyde (1:1), 250 °C	++++	0	+	0
glyoxal trimer/phenylalanine (0.33−1), 175 °C	+	0	0	0
glyoxal trimer/phenylalanine (1:1) 175 °C	+	0	0	0
glyceraldehyde/phenylalanine (1:1), 200 °C	+	0	+	0
glyceraldehyde/phenylalanine (1:1), 250 °C	0	++++	0	+
glyceraldehyde/phenylalanine (2:1), 250 °C	+++	0	+	0

[a] Based on chromatographic peak area per mole of phenylalanine. Values represent average of three replicates with percent standard deviation <15%. [b] Imine adduct with phenethylamine.

Table 2. Relative Amounts[a] of Phenylacetaldehyde, Phenethylamine, and Benzaldehyde Formed in Glucose/Phenylalanine Model Systems at 250°C

model system[b]	phenylacetaldehyde	phenethylamine	benzaldehyde	benzaldehyde-imine adduct[b]
glucose.phenylalanine (1:1)	**1**	0	**1**	0
glucose.phenylalanine (1:2)	0	45*x*	0	**1**
glucose.phenylalanine (1:1), air	1.6*x*	0	23*x*	0
glucose.phenylalanine (1:2), air	0	**1**	5*x*	38*x*

[a] Based on chromatographic peak area per mole of phenylalanine normalized relative to the lowest value in each column. Values represent average of three replicates with percent standard deviation <15%. [b] Imine adduct with phenethylamine.

attributed the formation of benzaldehyde to the generation of phenylpyruvic acid through transamination of phenylalanine in the reaction mixture. Due to the lack of systematic study on the thermal generation of benzaldehyde from phenylalanine, we provide evidence for its mechanism of formation using oxidative pyrolysis−GC-MS (*10*) and FTIR spectroscopy.

MATERIALS AND METHODS

All reagents and chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification.

Pyrolysis GC-MS Analysis. Py-GC-MS analyses were conducted using a Varian CP-3800 GC coupled with a Saturn 2000 ion trap mass spectrometry detector (Varian, Walnut Creek, CA). The pyrolysis unit included a CDS 1500 valved interface, and a CDS Pyroprobe 2000 unit (CDS Analytical, Oxford, PA) was installed onto the GC injection port. The GC was equipped with a sample preconcentration trap (SPT) filled with Tenax GR. About 1 mg of sample mixture was packed inside a quartz tube (0.3 mm thickness), plugged with quartz wool, and inserted inside the coil probe and pyrolyzed for 20 s at a temperature range from 175 to 250 °C. Liquid samples were mixed with silica gel in 1:10 ratio by weight. For the samples that were pyrolyzed in the presence of moisture, 3 μL of distilled water was added to the mix. The volatiles after pyrolysis were concentrated on the SPT at 50 °C for 4 min and subsequently desorbed at 100 °C to the GC column for separation. A DB-5MS capillary column (J&W Scientific, 50 m × 0.2 mm i.d; coating thickness = 0.33 μm) was used under the following conditions: a pressure pulse of 70 psi was set for the first 4 min and later maintained with a constant flow of 1.5 mL/min for the rest of the run regulated by an electronic flow controller (EFC).

Table 3. Amounts[a] of Benzaldehyde Formed from Different Precursors between 175 and 250°C Normalized Relative to Phenylethanediol System

model system	He	air	air/water
phenylacetaldehyde at 175 °C	12[b]	22[c]	536[c]
phenylacetaldehyde at 250 °C	51[b]	368[c]	**659**[c]
phenylethanediol at 175 °C	**1**	2	1.3
phenylethanediol at 250 °C	32	nd[d]	nd
phenethylamine/pyruvaldehyde (1:1) at 250 °C	0	nd	67
phenethylamine/pyruvaldehyde (1:0.5) at 250 °C	0	nd	50
phenylpyruvic acid, 175 °C	245	143	210
phenylglyoxal, 250 °C	20	48	127
phenylalanine at 200 °C	0	2	nd
phenylalanine/glucose[e] (1:1) at 250 °C	2	64	nd

[a] Based on chromatographic peak area per mole of precursor. Values represent average of two to three replicates with percent standard deviation <25%. [b] Preformed in the bottle during storage due to oxidation. [c] Corrected for residual benzaldehyde in phenylacetaldehyde by subtracting area/mol value of He experiments before normalization. [d] nd, not determined. [e] Based on area per mole of phenylalanine or glucose.

The GC oven temperature was set at −5 °C for 5 min using CO_2 as the cryogenic cooling source. Two temperature programs were used: (A) The temperature was increased to 100 °C at a rate of 50 °C/min and then to 180 °C at a rate of 5 °C/min. The oven temperature was

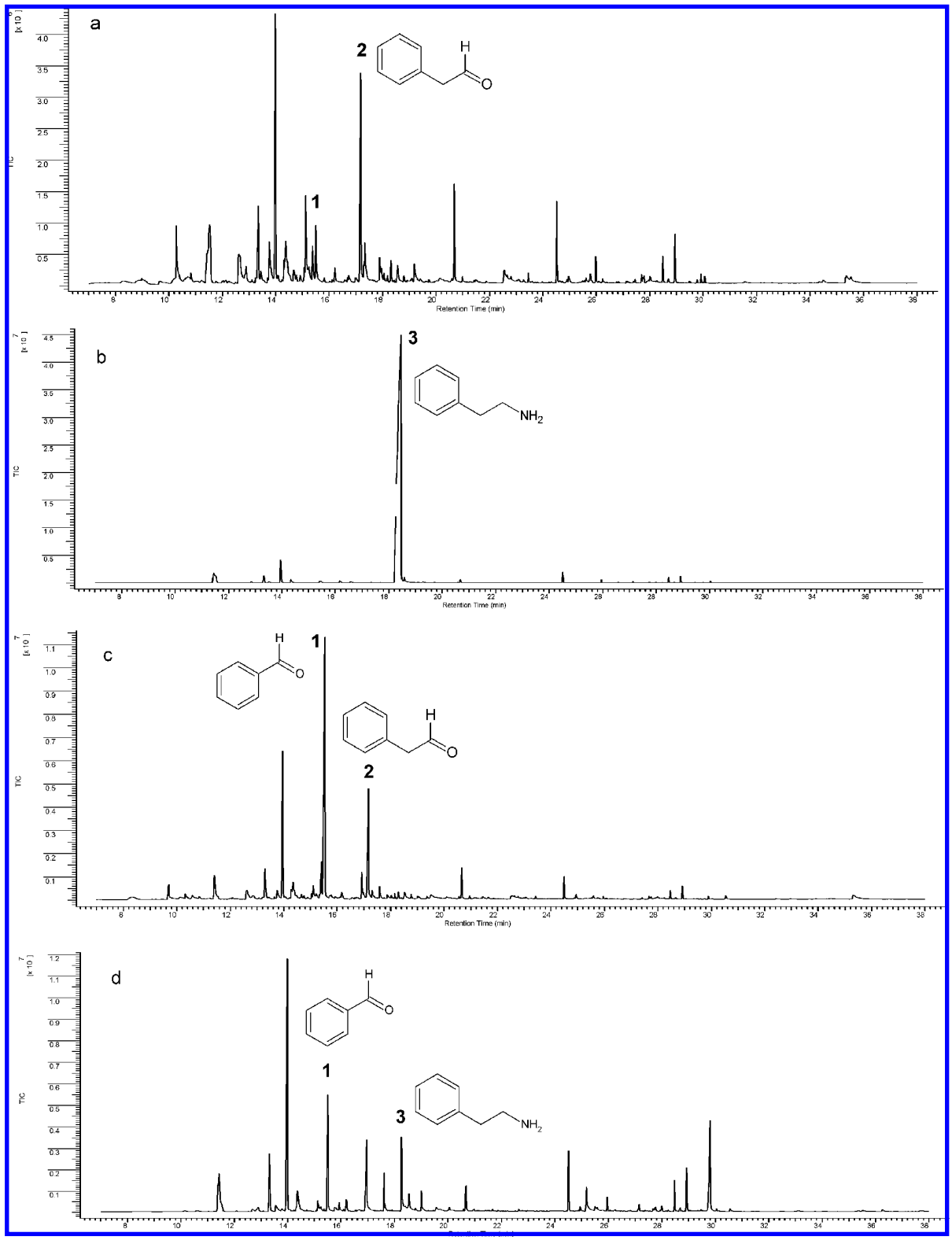

Figure 1. Pyrograms generated at 250 °C using temperature program B from (**a**) phenylalanine/glucose (1:1) under nonoxidative, (**b**) phenylalanine/glucose (2:1) under nonoxidative, (**c**) phenylalanine/glucose (1:1) under oxidative, and (**d**) phenylalanine/glucose (2:1) under oxidative conditions.

further increased to 280 °C at a rate of 20 °C/min and kept for 9.5 min (benzaldehyde elutes at 12.5 min). (B) The temperature was increased to 50 °C at a rate of 50 °C/min and then to 280 °C at a rate of 8 °C/min and kept for 5 min (benzaldehyde elutes at 15.5 min). MS data were collected using electron impact ionization mode under the following conditions: MS transfer line temperature, 250 °C; MS manifold temperature, 50 °C; MS ion trap temperature, 175 °C; ionization voltage, 70 eV; EMV, 1750 V; scan range, *m*/*z* 20−650. Compound identification was performed by using AMDIS (v2.62) and NIST Standard Reference Database (v05).

Oxidative or Wet Py-GC-MS Analysis. Pyrolysis under air or in the presence of moisture was achieved through modification of the above-mentioned GC to allow gas stream switching and subsequent isolation of the pyrolysis chamber from the analytical stream. The

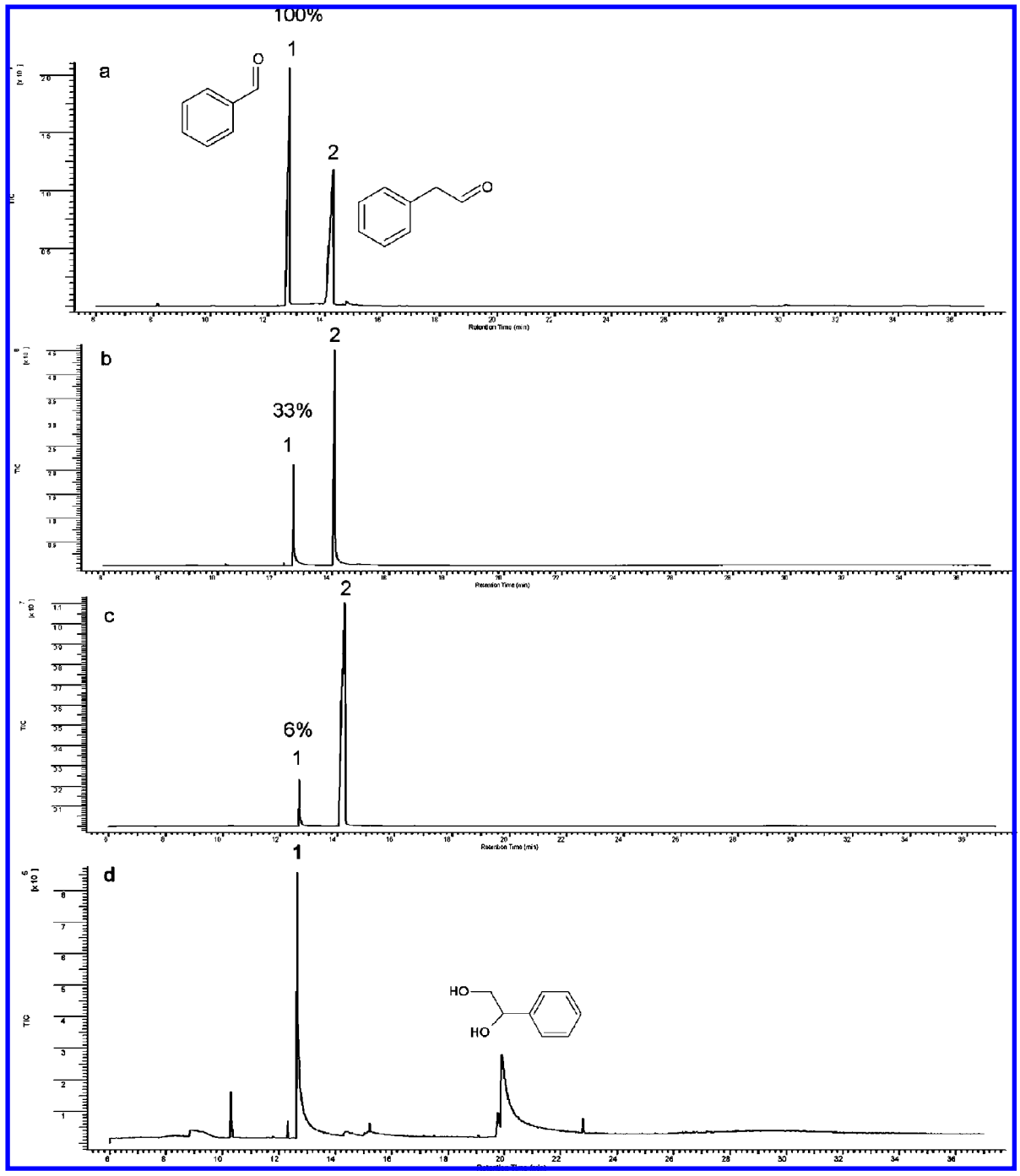

Figure 2. Pyrogram of phenylacetaldehyde (1 mg) generated at 175 °C under (**a**) wet/oxidative, (**b**) dry/oxidative, and (**c**) dry/nonoxidative conditions; (**d**) pyrogram generated through oxidative pyrolysis of 1-phenyl-1,2-ethanediol at 175 °C. Percentages represent areas of peak 1 (benzaldehyde) relative to peak 2 (phenylacetaldehyde). All above pyrograms were generated using temperature program A.

Table 4. Ability[a] of Phenylacetaldehyde To Generate Benzaldehyde Relative to the Listed Precursors under Optimum Conditions

model system	He	air	air/water
phenylethanediol at 175 °C		268	
phenylethanediol at 250 °C	20		
phenethylamine/pyruvaldehyde (1:1) at 250 °C			9.8
phenylpyruvic acid, 175 °C	2.1	3.7	2.5
phenylglyoxal, 250 °C	33	13.7	5.2
phenylalanine + glucose (1:1) at 250 °C	330	10.2	

[a] Relative to air/water values of phenylacetaldehyde reported in **Table 3**.

pyrolysates generated under air or in the presence of moisture were initially collected onto the trap, which retained the organic volatiles and vented the carrier gas (air) and/or moisture. The trap was subsequently flushed with helium and heated to desorb the collected volatiles. For details see Yaylayan et al. (*10*).

FTIR Monitoring of Oxidation Reactions. Pure samples such as benzaldehyde or phenylacetaldehyde were directly applied onto the ATR crystal and immediately scanned at either 35 or 100 °C. Infrared spectra were recorded on a Bruker Alpha-P spectrometer (Bruker Optic GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector, a temperature-controlled single-bounce diamond attenuated total reflectance (ATR) crystal, and a pressure application device for solid samples.

A phenylacetaldehyde oxidation mixture was prepared by dissolving 110 mg in 2 mL of acetonitrile, 25 μL of water, and 60 mg of 1,1′-azobis(cyclohexanecarbonitrile) 98% as a free radical initiator. After

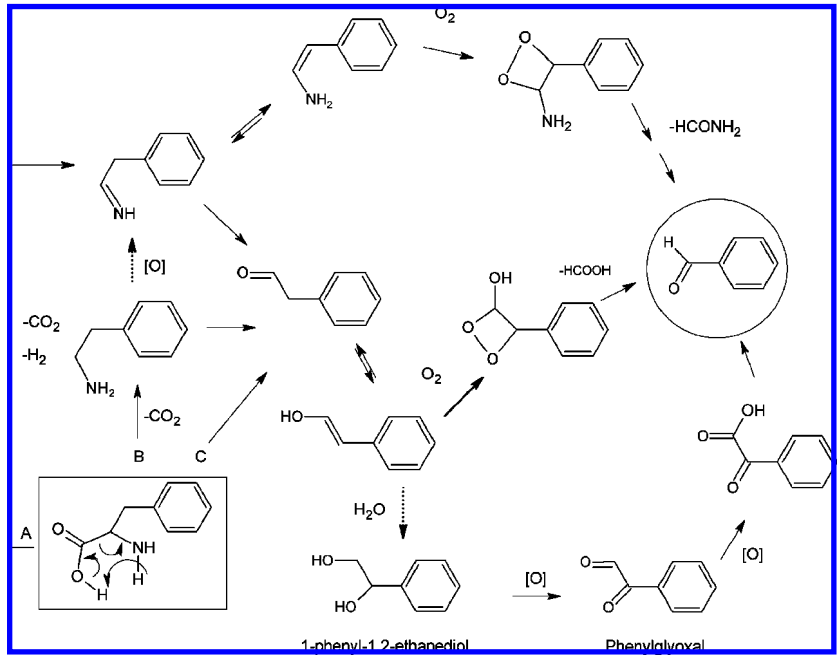

Figure 3. Proposed mechanisms of formation of benzaldehyde from phenylalanine: pathway A, oxidative decarboxylation; pathway B, thermal decarboxylation; pathway C, Strecker or imine isomerization pathway.

all of the components had dissolved, 50 μL was applied onto the ATR crystal and scanned at 100 °C for 1 h after evaporation of the solvent. The spectra were acquired at the specified temperature every 120 s for 60 min. A total of 32 scans at 4 cm^{-1} resolution were co-added. Processing of the FTIR data was performed using Bruker OPUS software.

RESULTS AND DISCUSSION

Different precursors have been proposed in the literature as possible sources of benzaldehyde in phenylalanine-containing model systems. However, no systematic study has been performed on the mechanism of thermal generation of benzaldehyde. To assess the potential of benzaldehyde generation from phenylalanine and to identify the role of phenylalanine degradation products such as Strecker aldehyde and Strecker amine, various model systems (see **Tables 1**−**3**) were reacted under oxidative and nonoxidative conditions and in the presence and absence of moisture using oxidative Py-GC-MS analysis, and the formation of benzaldehyde and its precursors phenylacetaldehyde and phenethylamine was monitored. The data indicated that in sugar/phenylalanine model systems the reaction generated either phenylacetaldehyde or phenethylamine depending on the ratio of the starting sugar to phenylalanine (see **Figure 1** and **Tables 1** and **2**) and that benzaldehyde was present in all systems in which phenylacetaldehyde was generated. When the sugar to phenylalanine ratio was ≥2:1, only phenylacetaldehyde was detected and not phenethylamine (except in the case of glucose). When the sugar to phenylalanine ratio was ≤1:1, only phenethylamine was detected (except in the case of glucose). Interestingly, phenylalanine alone also generated benzaldehyde under oxidative pyrolysis. It seems excess starting aldehyde/sugar prevents trapping of phenylacetaldehyde as an imine adduct by providing other carbonyl functional groups to scavenge the reactive amines including the phenethylamine, thus allowing free phenylacetaldehyde to be detected. The ability of glucose to degrade into molar excess of smaller aldehydes and ketones can explain the above exception observed with glucose. On the other hand, phenethylamine was detected only under nonoxidative conditions when the phenylalanine to sugar ratio was ≥2:1. Under these conditions neither phenylacetaldehyde nor benzaldehyde was observed. However, under oxidative conditions both phenylacetaldehyde and benzaldehyde were detected whether the phenylalanine to glucose ratio was 1:1 or ≥2:1. Furthermore, benzaldehyde concentrations were much higher in the presence of air, which indicated oxygen was involved in the reaction (see **Tables 2** and **3**). According to **Table 2**, in the glucose/phenylalanine (1:1) model system there was a 23-fold increase in benzaldehyde formation in the presence of air. A similar increase was noted in the model system when the glucose to phenylalanine ratio was 1:2; however, in this case benzaldehyde was trapped as the phenethylamine adduct. **Table 3** also indicates significant increases in benzaldehyde content when different precursors were pyrolyzed under air. In addition, water seemed to play an important role in enhancing benzaldehyde formation from phenylacetaldehyde. For example, at 175 °C under wet oxidative pyrolysis, phenylacetaldehyde produced an almost 24-fold excess of benzaldehyde relative to dry oxidative pyrolysis. **Figure 2**, panels **a** and **b**, demonstrates the role of wet and dry oxidative pyrolysis of phenylacetaldehyde in the generation of benzaldehyde relative to dry nonoxidative pyrolysis (**Figure 2c**). Detection of a small amount of benzaldehyde in phenylacetaldehyde during nonoxidative pyrolysis indicates its facile oxidation into benzaldehyde during storage. Inspection of **Table 3** also reveals that there is more than one precursor of benzaldehyde and that phenylacetaldehyde is the most efficient precursor followed by phenylpyruvic acid. Phenylalanine, phenethylamine, phenylglyoxal, and phenylethanediol all can generate benzaldehyde, and all require oxidative conditions except phenylpyruvic acid, which does not require air, but the presence of water enhances its formation, indicating the possible existence of oxidative and nonoxidative pathways of benzaldehyde generation depending on the precursor. According to **Table 3**, phenylalanine and phenylethanediol have comparable abilities to generate benzaldehyde between 175 and 200 °C under oxidative conditions. The phenylalanine/glucose model sys-

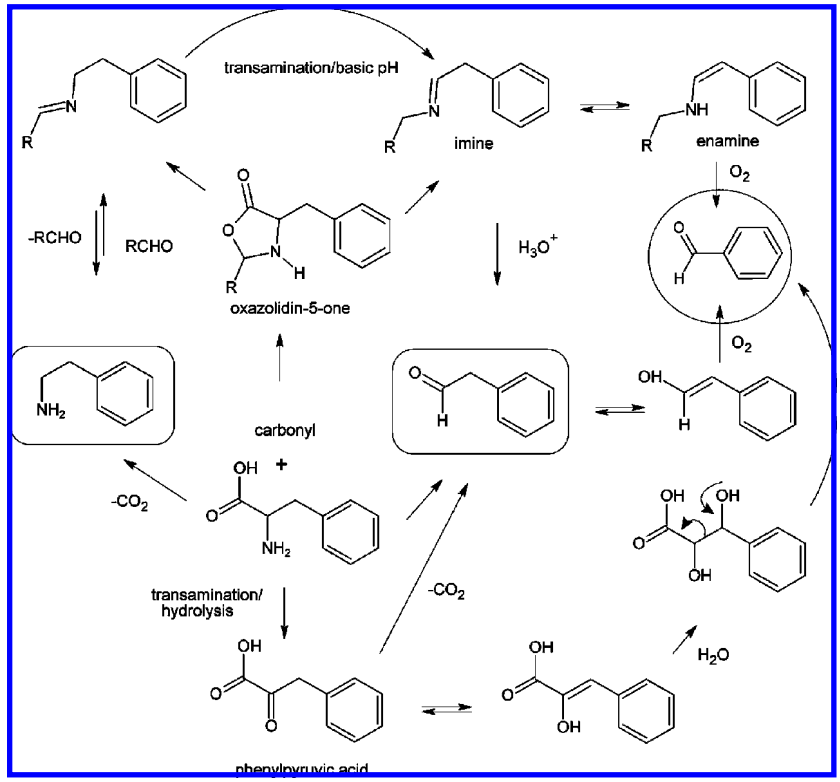

Figure 4. Proposed formation pathways of benzaldehyde precursors from phenylalanine.

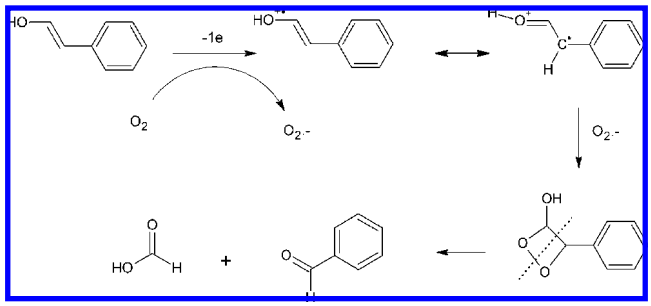

Figure 5. Proposed mechanism of free radical initiated oxidation of phenylacetaldehyde from its enol form.

tem, on the other hand, showed ability comparable to that of the phenethylamine/pyruvaldehyde system. **Table 4** summarizes the ability of phenylacetaldehyde to generate benzaldehyde relative to other precursors. According to this table phenylacetaldehyde has a 2−3-fold higher ability to generate benzaldehyde relative to phenylpyruvic acid.

According to **Figure 3** phenylalanine can generate phenylacetaldehyde through three pathways: oxidative decarboxylation (*11*) followed by hydrolysis (pathway A) or thermal decarboxylation (pathway B) or the Strecker reaction (pathway C). In addition, 1-phenyl-1,2-ethanediol, phenylglyoxal, and phenylglyoxylic acid theoretically can be generated from the oxidation and/or hydration of phenylacetaldehyde as proposed in **Figure 3**, and they are found to be also possible precursors of benzaldehyde as mentioned above (see **Table 3**). Furthermore, as reported by Granvogl et al. (*5*), the formation of benzaldehyde was also observed in the mixtures of phenethylamine and pyruvaldehyde, which was corroborated in this study (see **Table 3**). According to **Figure 4**, phenethylamine could be formed from phenylalanine either through thermal decarboxylation or through oxazolidin-5-one formation (*12*) in the presence of sugar or carbonyl compounds. In addition, transamination of phenylalanine (*12*) can also generate another important precursor of benzaldehyde, the phenylpyruvic acid.

Proposed Mechanism of Benzaldehyde Formation from Phenylacetaldehyde. Although phenylalanine can generate different precursors that are able to form benzaldehyde, phenylacetaldehyde, the Strecker aldehyde, is the most efficient and established precursor. In converting phenylacetaldehyde into benzaldehyde, an oxygen atom should be introduced at the benzylic carbon and the carbon−carbon bond should be cleaved. Free radical initiated oxidative cleavage of the carbon−carbon double bond of the enolized phenylacetaldehyde can serve as a suitable mechanism for this transformation (see **Figure 5**). This mechanism is based on the findings of Tokunaga et al. (*13*). They identified molecular oxygen as a convenient oxidizing agent able to oxidize the carbon−carbon double bond of enol ethers into alkyl formate and an aldehyde (or ketone). This oxidation was catalyzed either by Brønsted acids or preferably by $CuCl_2$ at 40 °C. Previously, Kaneda et al. (*14*) also reported on the ability of molecular oxygen to similarly oxidize a structurally related class of compounds, the enamines. We therefore propose that enols similar to enamines or enol ethers can undergo oxidation by a single electron transfer to molecular oxygen and the formation of enol radical cation and a superoxide anion as shown in **Figure 5**. In the case of phenylacetaldehyde the enol radical cation is further stabilized through resonance by the formation of a benzylic radical in which the cation is also stabilized as an oxonium ion (see **Figure 5**). The resulting superoxide radical can then react with the enol radical cation and generate the known 1,2-dioxetane ring structure capable of thermal cleavage into benzaldehyde and formic acid (*13, 15, 16*). The temperature dependence of benzaldehyde formation was already demonstrated above (see **Table 3**). Supporting evidence for the

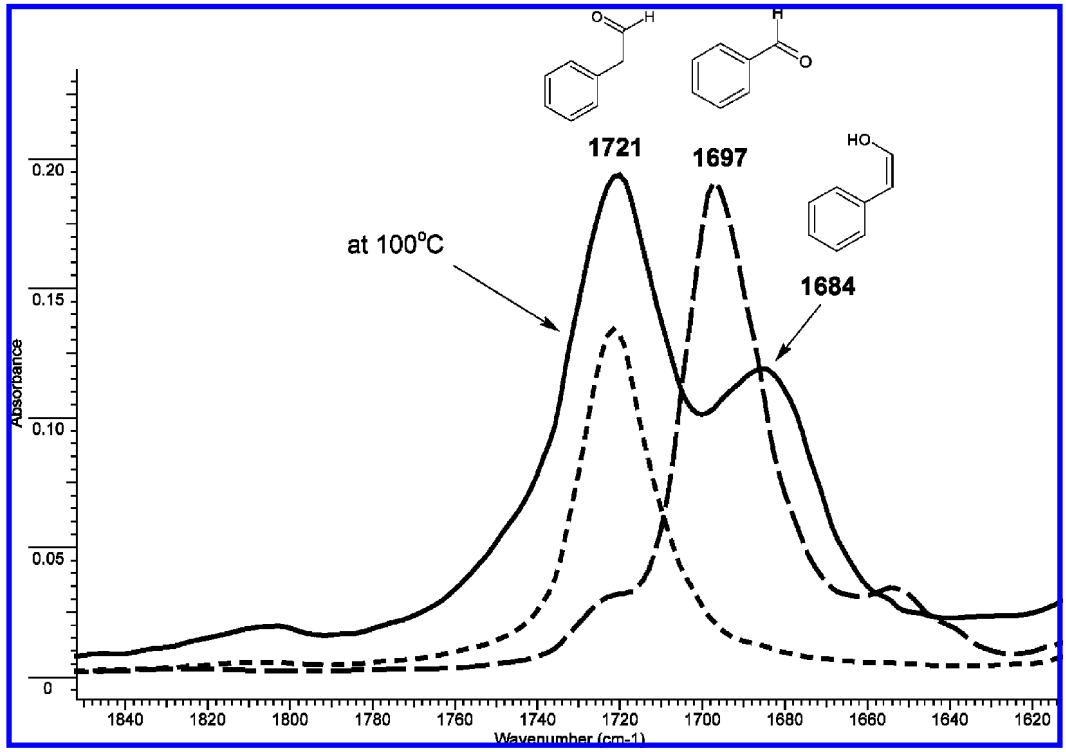

Figure 6. FTIR spectra of phenylacetaldehyde (- - -), benzaldehyde (— —) acquired at 35 °C, and phenylacetaldehyde acquired at 100 °C (—).

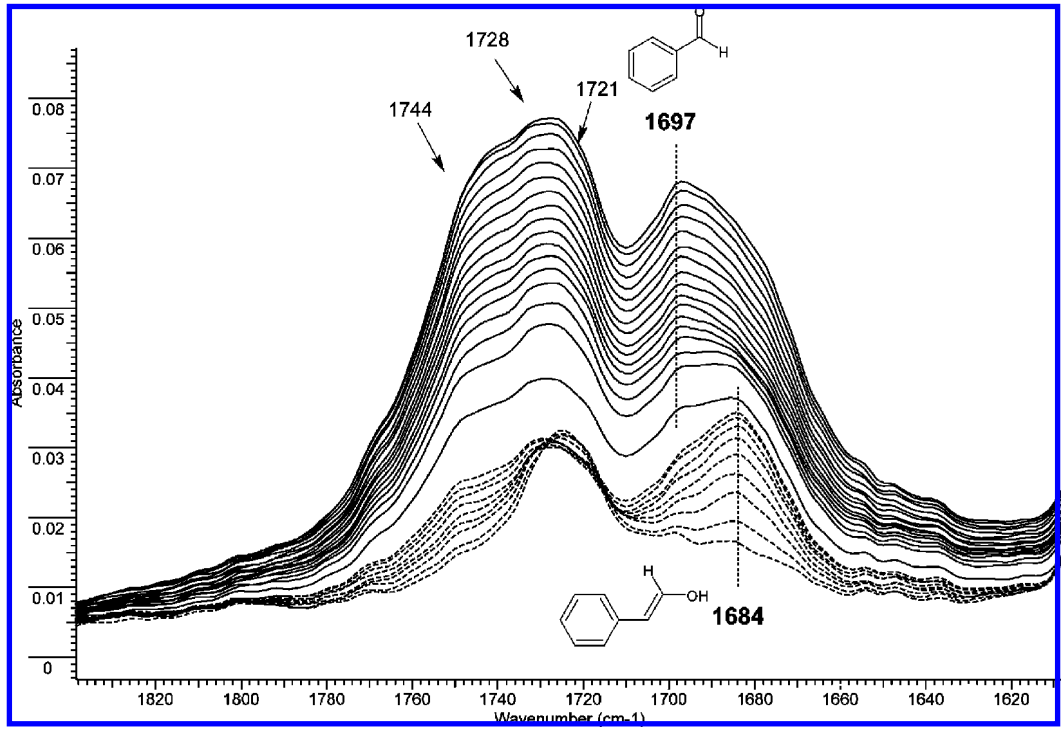

Figure 7. Time-dependent spectra of phenylacetaldehyde oxidation catalyzed by 1,1′-azobis(cyclohexane-carbonitrile) acquired at 100 °C over 1 h scanned at 2 min intervals. Dotted spectra represent the first 18 min, and solid line spectra represent the remaining 42 min.

proposed mechanism was provided through FTIR monitoring of the evolution of the benzaldehyde band centered at 1697 cm^{-1} from heated phenylacetaldehyde in the presence and absence of 1,1′-azobis(cyclohexanecarbonitrile), a free radical initiator on an ATR crystal. **Figure 6** shows the aldehyde absorption bands of benzaldehyde and phenylacetaldehyde centered at 1697 and 1721 cm^{-1}, respectively. To initiate enolization, the spectrum of phenylacetaldehyde was acquired at 100 °C, and as shown in **Figure 6**, the enol band appeared at 1684 cm^{-1}. Having assigned the characteristic bands needed to monitor the oxidation process, the phenylacetaldehyde was heated at 100 °C on an ATR crystal over a period of 1 h and scanned at 2 min intervals. As shown in **Figure 7** in the presence of the free radical initiator, the enol band of phenylacetaldehyde at 1684 cm^{-1} formed and increased over a period of 18 min. After this initial buildup of the band at 1684 cm^{-1}, a new band centered at 1697 cm^{-1} (benzaldehyde) appeared and increased over time at the expense of

the enol band of phenylacetaldehyde, indicating conversion of enol into benzaldehyde. In the absence of free radical initiator the characteristic bands were of lower intensities.

Proposed Mechanism of Benzaldehyde Formation from Other Precursors. *Phenylalanine and Phenylpyruvic Acid.* According to **Table 3**, pyrolyzing phenylalanine by itself at 200 °C under oxidative condition also produces benzaldehyde. **Figure 3** illustrates the proposed mechanism whereby phenylalanine undergoes oxidative decarboxylation to form phenethylimine (pathway A in **Figure 3**), which can be hydrolyzed into phenylacetaldehyde followed by oxidation and formation of benzaldehyde as shown above; alternatively, it can isomerize into enamine and undergo oxidation (*14*) to benzaldehyde, similar to phenylacetaldehyde as depicted in **Figure 5**. In the presence of carbonyl compounds, phenylalanine can undergo transamination and generate phenylpyruvic acid (*6, 12*). Although this intermediate theoretically can decarboxylate and form phenylacetaldehyde as a precursor of benzaldehyde, as shown in **Table 3**, the amount of benzaldehyde was not affected much when it was pyrolyzed under oxidative condition. A nonoxidative pathway based on water addition followed by retro-aldol cleavage is proposed in **Figure 4**.

1-Phenyl-1,2-ethandiol/Phenylglyoxal/Phenylglyoxylic Acid. In the presence of water, the enol form of phenylacetaldehyde can undergo Markovnikov addition of water to generate 1-phenyl-1,2-ethanediol followed by successive oxidations to generate first the enediol (2-hydroxy-1-phenylethanone and/or 2-hydroxyl-2-phenyl acetaldehyde), followed by phenylglyoxal, and finally phenylglyoxylic acid formation (see **Figure 3**). The decarboxylation of the latter hypothetically can yield benzaldehyde. When commercially available 1-phenyl-1,2-ethanediol and phenylglyoxal were pyrolyzed under oxidative conditions (see **Figure 2d**), they both generated more benzaldehyde compared to nonoxidative conditions, indicating thermal cleavage of *gem*-diols can also produce an aldehyde.

Phenethylamine. Granvogl et al. (*5*) proposed a multistep mechanism for the formation of benzaldehyde from a heated mixture of phenethylamine and pyruvaldehyde based on imine isomerization, oxidation, and water addition steps. According to **Figure 4**, the formation of phenethylamine Schiff base with any carbonyl compound followed by transamination can generate an imine that can either hydrolyze into phenylacetaldehyde or isomerize into enamine; both are capable of being oxidized into benzaldehyde as depicted in **Figure 5**. As shown in **Table 3**, nonoxidative conditions did not generate any benzaldehyde.

Different precursors generated from phenylalanine therefore can form benzaldehyde in Maillard model systems; however, phenylacetaldehyde can be considered to be the major precursor under oxidative conditions, and phenylpyruvic acid can be considered to be the major precursor under nonoxidative conditions. The corresponding 4-hydroxybenzaldehyde identified in tyrosine model systems incubated under physiological conditions (*17*) could also have an origin similar to that of benzaldehyde.

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