Formation Kinetics of 2,5-Dimethylpyrazine and 2-Methylpyrazine in a Solid Model System Consisting of Amioca Starch, Lysine, and Glucose

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A new analysis using the fractional conversion technique was applied to determine the formation kinetics of 2,5-dimethylpyrazine and 2-methylpyrazine in a solid model system containing 4.5% (w/w) lysine, 5.5% glucose, and amioca starch with 10% moisture (dry basis) from 80 to 120 °C. The reaction order and kinetic parameters (rate constants and activation energy) were determined through a parameter estimation technique based on least-squares fit. The formation rate of both pyrazines followed a first-order reaction model. No significant differences were observed for the activation energies and rate constants for 2,5-dimethylpyrazine and 2-methylpyrazine, suggesting the production of these pyrazines was controlled by the same rate-limiting step. The activation energy was 13.5 kcal/mol.

Keywords: *Kinetics; 2,5-dimethylpyrazine and 2-methylpyrazine; solid state; fractional conversion*

INTRODUCTION

The quality of a food product depends on the attributes present in the final product. The process parameters and extent of processing determine the final quality of the product. Knowledge of the kinetic parameters of a chemical reaction, such as reaction order, rate constant, and activation energy, is essential for predicting quality changes during thermal processing.

The Maillard reaction is responsible for flavor and color development in many thermally processed foods. However, most kinetic studies of the Maillard reaction have been associated with color formation. Maillard browning reactions have been reported to follow a pseudo-zero-order reaction when the absorbance at 420 nm was measured to monitor the extent of the reaction as a function of time (Warmbier et al., 1976a,b; Labuza and Saltmarch, 1981; Saltmarch et al., 1981; Weissman et al., 1993; Peterson et al., 1994).

The kinetics of flavor formation in solid foods is important for the optimization of many thermal processes such as extrusion, baking, roasting, frying, and drying. Pyrazines have been found to be a major class of compounds formed by the Maillard reaction in these processes (Bailey et al., 1994; Nair et al., 1994). They are important aroma compounds responsible for roasted, toasted, and nutty notes in many foods (Maga, 1992). The substantial interest generated by pyrazines as important flavor compounds in thermally processed foods has resulted in many studies on the effects of various factors and the mechanism of pyrazine formation (Koehler et al., 1969; Rizzi, 1972; Shibamoto and Bernhard, 1976, 1977) and has stimulated the need for kinetic research to quantify pyrazine formation.

Leahy and Reineccius (1989a) studied the effect of amino acid and sugar on the formation kinetics of alkylpyrazines in an aqueous model system. Equimolar concentrations (0.1 M) of the amino acid and sugar were heated in a pH 9 buffered solution at 75, 85, and 95 °C. Pyrazine formation was found to fit a pseudo-zero-order model. The activation energies for alkylpyrazines ranged from 27 to 45 kcal/mol, with the dimethylpyrazines having slightly higher activation energies than pyrazine and 2-methylpyrazine.

In a separate study, Leahy and Reineccius (1989b) investigated the effects of pH and water activity on the kinetics of pyrazine formation. Pseudo-zero-order was used to model pyrazine formation rate. An aqueous model system and nonfat dry milk (NFDM) were used as food models. The rates of pyrazine formation increased with pH up to 9 and with water activity up to 0.75. Activation energies were reported between 33 and 45 kcal/mol.

Huang et al. (1989) studied the kinetics of pyrazine formation in aqueous model systems containing equimolar amounts of amino acids and glucose (0.028 M) at pH 10 from 120 to 140 °C. The authors reported pseudo-zero-order reaction kinetics for the formation of pyrazines with activation energies ranging from 19.5 to 29 kcal/mol depending upon the amino acid.

Recently, Huang et al. (1995) studied the kinetics of tetramethylpyrazine formation under high hydrostatic pressure in aqueous, 80% propylene glycol (PG) and ethanol model systems from the reaction of 0.01 M 3-hydroxy-2-butanone and 0.03 M ammonium salt. The reaction followed a pseudo-zero-order kinetics for all systems with activation energies of 18.84 ± 1.3 kcal/mol for the aqueous system, 14.19 ± 7.1 kcal/mol for the 80% PG system, and 13.09 ± 4.7 kcal/mol for the ethanol system.

Most of the kinetic studies on pyrazine formation have been limited to aqueous model systems. To simulate pyrazine formation in foods during various industrial processes, it is necessary and more desirable to study the kinetics of pyrazine formation in solid systems since the kinetic parameters and the analytical procedures can be quite different between solids and aqueous solutions. Therefore, the objective of this study was to

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S0021-8561(96)00819-9 CCC: $14.00

reevaluate the analysis in determining the kinetic parameters of a reaction system as complex as pyrazine formation and to develop a new technique to predict the formation of 2-methylpyrazine and 2,5-dimethylpyrazine as a function of time and temperature in a solid model food system.

THEORETICAL CONSIDERATIONS

For a unimolecular irreversible chemical reaction with a known mechanism, A → P, the rate equation is

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A]^n = k([A_0] - [P])^n \quad (1)$$

where $[A_0]$ is the reactant concentration at time 0, [A] is the reactant concentration at time t, [P] is the product concentration at time t, t is the reaction time, k is the rate constant, and n is the reaction order.

For a true zero-order degradation reaction, $n = 0$, the rate equation (1) reduces to

$$-\frac{d[A]}{dt} + k \quad (2)$$

Upon integration, eq 2 becomes

$$[A_t] - [A_0] = -kt \quad (3)$$

A plot of the reactant concentration versus time is linear with a slope equal to $-k$. Equation 2 indicates that the rate of the degradation reaction is independent of the reactant concentration.

When the rate of product formation follows a true zero-order reaction, the following expression can be obtained from eq 1:

$$\frac{d[P]}{dt} + k \quad (4)$$

Upon integration, the expression becomes

$$[P_t] - [P_0] = kt \quad (5)$$

Equation 5 also indicates that the plot of product concentration versus time is linear with a slope of k and that the rate of product formation is independent of the reactant concentration.

When $[A_0] \gg [P]$, the rate equation (1) can be reduced to

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k[A_0]^n \quad (6)$$

Since the term $[A_0]^n$ is a constant, it can be grouped with the rate constant, k, as part of the apparent rate constant, k', as follows:

$$k' = k[A_0]^n \quad (7)$$

Replacing into eq 6 gives

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k' \quad (8)$$

A reaction when its rate follows eq 8 is known as a pseudo-zero-order reaction. Integrating eq 8 for product formation gives an expression similar to eq 5:

$$[P_t] - [P_0] = k't \quad (9)$$

A plot of product concentration versus time also yields a straight line with a slope of k'. The product concentration as a function of time and thus the slope of the plot are always independent of the initial concentration of the reactant for a true zero-order reaction. Nevertheless, the slope of the plot increases when the initial reactant concentration is increased for a pseudo-zero-order reaction.

For a first-order degradation reaction, $n = 1$, the rate equation (1) becomes

$$-\frac{d[A]}{dt} = k[A] \quad (10)$$

Integration of eq 10 yields

$$\ln([A]/[A_0]) = -kt \quad (11)$$

The plot of the logarithm of $[A]/[A_0]$ versus time is a straight line with a slope equal to $-k$.

The rate of product formation for a first-order reaction is as follows:

$$\frac{d[A]}{dt} = k[A] = k([A_0] - [P]) \quad (12)$$

Upon integration, the expression becomes

$$\ln[([A_0] - [P])/[A_0]] = -kt \quad (13)$$

Therefore, the plot of the logarithm of $[A_0] - [P]$ versus time would be a straight line with a slope of $-k$.

When the formation of products resulting from the reactions of an amino acid and a sugar is observed to follow a pseudo-zero-order kinetic model, it suggests that the reactants are in excess. In other words, the initial reactant concentrations are so high that the amount of reactants reacted to form the products during the entire period of study does not significantly change the initial reactant concentrations. Nevertheless, studies with respect to nonenzymatic browning reaction in model systems consisting of an amino acid and a sugar have shown significant losses of the reactants with respect to time, even though the reaction has generally been recognized to follow a zero-order reaction. Lee et al. (1984) showed a 50% degradation of lysine after 1 h of heating with glucose in 80% methanol at 69 °C, while pigment formation was not visible until after 2 h of heating. Warmbier et al. (1976a) studied nonenzymatic browning in an intermediate moisture solid model system at storage temperatures (25−45 °C) and reported that as much as one-third of the glucose and 70% of the lysine reacted before browning was observed. The authors stated "a significant amount of glucose and available lysine are destroyed even before pigment production becomes appreciable". Warmbier et al. (1976b) also showed more than a 50% loss for both glucose and lysine in an intermediate moisture model system held at 45 °C for 20 days. The authors reported that each of the reactants followed first-order reaction kinetics as corroborated by other studies (Labuza and Baisier, 1992) and concluded that the glucose/amine condensation step did not control the rate of pigment formation.

Equations 1−13 were derived on the basis of the assumption that the reaction is a simple irreversible process with a known mechanism. They may not be applicable to model the formation rate of pyrazines since the production of pyrazines involves many steps (Shiba-

moto and Bernhard, 1977) and the exact mechanisms are yet to be elucidated. Even though the pseudo-zero-order model has been widely used, its adequacy needs to be further validated, especially when the reaction temperature is high and the reaction time is long. Recently, brown color formation in solid foods at elevated temperatures during baking and frying was found to fit the first-order, instead of zero-order, kinetic model when the fractional conversion technique was applied (Ateba and Mittal, 1994; Zanoni et al., 1995).

The fractional conversion technique has been used extensively in chemical engineering (Levenspiel, 1972; Hill, 1977) as an accurate method of correlating the extent of a chemical reaction with the measurement of a physical property. To determine the reaction kinetics, it is essential to know the extent of the reaction at any time. The extent of pyrazine formation at any time or the fractional conversion, f, at a constant temperature can be described as

$$f = \frac{\text{amt of product (pyrazine) formed}}{\text{max amt of product (pyrazine) that can be produced}} \quad (14)$$

When the pyrazine concentration as a function of time is known, f can be defined as

$$f = \frac{[C_t] - [C_0]}{[C_\infty] - [C_0]} \quad (15)$$

where $[C_0]$ is the initial pyrazine concentration at time 0, $[C_t]$ is the pyrazine concentration at time t, and $[C_\infty]$ is the pyrazine concentration when the reaction time is long enough so that the reaction is completed and it can be temperature dependent.

For a reaction that follows a first-order kinetic model, the following expression can be obtained (Levenspiel, 1972):

$$\ln\left(\frac{[C_\infty] - [C_t]}{[C_\infty] - [C_0]}\right) = \ln(1 - f) = -kt \quad (16)$$

Therefore, the plot of the natural logarithm of $(1 - \times a6)$ versus time would yield a straight line with a slope equal to $-k$.

The temperature dependence of the rate constant normally follows the Arrhenius equation

$$\ln k = \ln[A_0 - (E_a/RT)] \quad (17)$$

where A_0 is the pre-exponential constant, E_a is the activation energy (cal/mol), R is the universal gas constant (1.987 cal/mol), and T is the temperature in degrees Kelvin.

Equation 16 can be arranged to give the following:

$$[C_t] = [C_\infty] + ([C_0] - [C_\infty]) \exp(-kt) \quad (18)$$

Equations 17 and 18 can be combined to predict pyrazine concentration as a function of time and temperature when the pre-exponential constant and the activation energy are known. In the case that C_∞ is temperature dependent, a correlation or mathematical model is also required to relate C_∞ to temperature.

MATERIALS AND METHODS

Preparation of the Model System. The solid model system was prepared according to the following procedure: (1) 1000 g of amioca starch (National Starch and Chemical Co., Bridgewater, NJ) was mechanically mixed with 50 g of L-lysine and 60 g of α-D-glucose (both from Aldrich Chemical Co., Milwaukee, WI) dissolved in 1000 mL of distilled water to form a viscous paste; (2) the mix was freeze-dried in a freeze-drier (F. J. Stokes Machine Co., Philadelphia, PA) to approximately 4% moisture content, dry basis (db); and (3) a calculated amount of water was added back to the freeze-dried mix, which was accomplished by using a fine mist spray with continuous mixing to obtain a final moisture content of 10% (db). The sample was sealed in home canning jars and stored at −20 °C until use. The prepared sample had a final composition of 4.5% (w/w) lysine and 5.5% (w/w) glucose corresponding to equimolar amounts of reactants.

Kinetic Studies. Silanized glass ampules (5 mL) were packed (Wheaton, Inc., Millville, NJ) to contain 4.53 g of the model system and plugged with silanized glass wool (Supelco, Inc., Bellefonte, PA) to keep a constant sample porosity (ϕ) of 0.5. Sample porosity is defined as

$$\phi = 1 - (\rho_b/\rho_s) \quad (19)$$

where ρ_b and ρ_s are bulk and solid density, repectively.

The ampules were flame sealed and heated in a constant-temperature circulating oil bath (MGW Lauda C20-CS, Brinkman Instruments, Westbury, NY) at the desired temperatures. The ampules were removed at predetermined time intervals, cooled immediately in an ice bath, and stored at −20 °C until quantification of the desired flavor compounds. A sample for zero time was taken immediately after the come-up time, which was estimated to be approximately 10 min in the temperature range of interest. Experiments were run at 80, 90, 100, 110, and 120 °C in duplicate.

Since the concentrations of 2-methylpyrazine and 2,5-dimethylpyrazine in the heated food model were lower at lower temperatures, four heated ampules (18 g of the solid model system) were combined for experiments conducted at 80, 90, and 100 °C and two heated ampules were combined for the 110 and 120 °C experiments before solvent extraction.

Pyrazine Isolation and Quantification. Fifty milliliters of methylene chloride (*Optima,* Fisher Scientific, Springfield, NJ) and 100 μg of pyrimidine (Aldrich) as the internal standard were added to a heated samples for extraction at room temperature for 72 h on the basis of the findings by Jusino (1996). The sample was filtered through Whatman No. 1 filter paper (Fisher Scientific). The solids were recovered from the filter paper and extracted using 50 mL of methylene chloride with continuous stirring for 20 min at room temperature. The extract was combined with the first extract. The solids were recovered, extracted with 50 mL of methylene chloride for 20 min a second time, and filtered. The extract was combined with the previous two extracts and dried over anhydrous sodium sulfate (Fisher Scientific) to remove water. The anhydrous extract was filtered through Whatman No. 2 filter paper and concentrated in a Kuderna-Danish (KD) concentration apparatus (Supelco) in a constant-temperature circulating water bath (DC5-W15, Haake Buchler Instruments, Kansas City, MO) at 55 °C to 5 mL. The concentrate was further reduced to 0.1 mL under nitrogen flow and then analyzed by gas chromatography (GC) for 2-methylpyrazine and 2,5-dimethylpyrazine concentration using calibration curves constructed on the same day. Tentative identification of 2-methylpyrazine and 2,5-dimethylpyrazine peaks was accomplished by comparing the chromatograms of samples with those spiked with pure concentrated standards.

Calibration curves were constructed as described by Jusino (1996). A series of standard solutions, in the range of 0−100 ppm, containing a constant pyrimidine (internal standard) concentration of 100 ppm were used to construct the calibration curves. In this study, concentration of pyrazine were reported in parts per million (ppm).

GC Analysis. A HP 5890A GC (Hewlett-Packard Co., Santa Clara, CA), equipped with a hydrogen flame ionization detector (FID) and a nonpolar fused silica capillary column (DB-1, 60 m × 0.32 mm i.d., 1.05 μm film thickness, J&W Scientific Co., Folsom, CA) and operated at a split ratio of 10:1, was used to analyze and quantify the concentrations of the

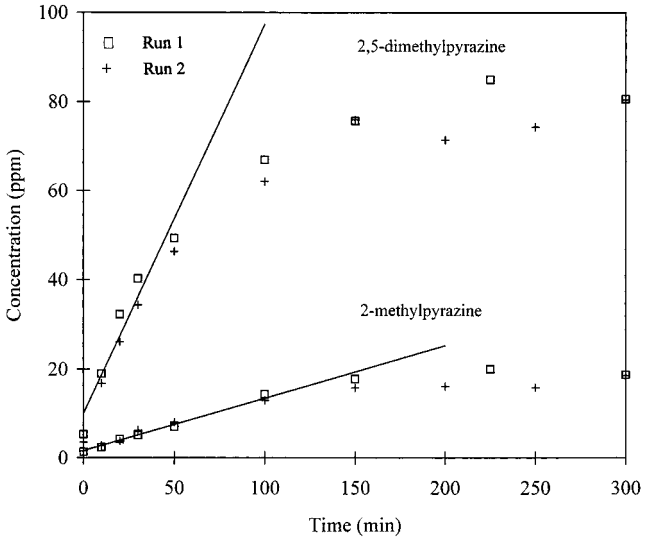

Figure 1. Formation of 2-methylpyrazine and 2,5-dimethylpyrazine at 90 °C.

flavor compounds. The GC was programmed to increase from an initial temperature of 50 °C to a final temperature of 250 °C at a heating rate of 2 °C/min. The injector temperature was 270 °C, and the detector temperature was 300 °C. The flow rate of the helium carrier was 1.2 mL/min.

Measurement of Glucose Concentration. The solid model system sealed in ampules was heated in an oil bath at 90 °C for 30 and 120 min. The samples were removed, immediately cooled in an ice bath, and stored at −20 °C until analysis. Unheated samples were also analyzed and served as the controls. Two grams of each sample was extracted with 100 mL of distilled water and filtered through Whatman No. 42 filter paper.

A glucose analysis kit from Sigma Diagnostics (Procedure 510, Sigma) along with a spectrophotometer (Spectronic 301, Milton Roy Co., Rochester, NY) at 442 nm, which was previously determined to give the highest absorbance, was used to determine the glucose concentrations in the water extracts. The Sigma procedure is essentially that of Raabo and Terkildsen (1960) for the determination of blood glucose. The analysis is a colorimetric method in which the sample solution is added to a mixture of the enzymes glucose oxidase and peroxidase and the chromogen *o*-dianisidine. The reaction produces an oxidized *o*-dianisidine which appears brown in color. The intensity of brown color measured at 425−475 nm is proportional to the glucose concentration.

RESULTS AND DISCUSSION

The model system was designed to contain equimolar amounts of lysine and glucose of approximately 0.03 mol/100 g of starch. 2-Methylpyrazine and 2,5-dimethylpyrazine were chosen for the kinetic studies because they have been found to play an important role in the characteristic aroma of roasted foods (Koehler et al., 1971).

The concentration of 2,5-dimethylpyrazine and 2-methylpyrazine in the heated model food system as a function of time at 90 °C is shown in Figure 1. Several observations can be readily made from this graph. The concentrations increased with time and then reached a plateau, indicating that the production of the pyrazines had come to completion, after prolonged heating. Although it appeared quite reasonable to model the formation of both pyrazines by the pseudo-zero-order kinetic model up to a reaction time of 40 min due to the linearity of the plot, the model completely failed to predict the curvilinear and plateau behavior of the experimental data. The rate constant (or the slope of the plot) for 2,5-dimethylpyrazine was almost 8 times that of 2-methylpyrazine (0.856 ppm/min for 2,5-dimethylpyrazine and 0.119 ppm/min for 2-methylpyrazine) if the pseudo-zero-order model had been applied for data analysis. 2,5-Dimethylpyrazine was produced not only at a higher rate but also to a greater plateau concentration (4−5 times greater), referred to as the maximal achievable or equilibrium concentration (C_∞), than 2-methylpyrazine. It is interesting to point out that the times at which the concentrations began to level off, referred to as the plateau time (around 150 min), were the same for both pyrazines. Although not shown here, a similar phenomenon was also observed at the other temperatures studied with the exception that the plateau times and equilibrium concentrations were temperature dependent: the higher the temperature, the shorter the plateau time and the higher the equilibrium concentration.

Table 1. Glucose Concentration of the Model System after Being Heated at 90 °C for 30 and 120 min

time (min)	glucose concentration (mg/g of sample)	time (min)	glucose concentration (mg/g of sample)
0	58.41 ± 3.36	120	7.20 ± 0.47
30	6.82 ± 0.73		

Table 1 shows the glucose concentration in the solid model system as a function of time at 90 °C. About 90% of the original glucose disappeared at or even before 30 min of heating and then remained unchanged. Lysine has been shown to react at a similar rate as glucose in a model system with a glucose/lysine molar ratio of 1.58 and a moisture content of 11.3% (db) (Warmbier et al., 1976b). From a comparison of Table 1 and Figure 1, which show that the concentrations of 2,5-dimethylpyrazine and 2-methylpyrazine were still increasing while the glucose concentration reached a plateau value, it was evident that an intermediate rate-limiting step existed that controlled the formation of pyrazines.

Since the pseudo-zero-order kinetic model could not describe the pyrazine concentrations over the entire expanse of the reaction, a different data reduction procedure and kinetic model, other than the pseudo-zero-order model, were necessary. The fractional conversion, f, can be easily defined and calculated by eq 15 when the concentration of a product as a function of time is known and it approaches a plateau value. The technique was then applied to determine the formation kinetics of 2,5-dimethylpyrazine and 2-methylpyrazine. The plots of the logarithm of the $1 - f$ versus time for 2,5-dimethylpyrazine ($r^2 = 0.974$) and 2-methylpyrazine ($r^2 = 0.966$) at 90 °C are shown in Figures 2 and 3, respectively. The linearity of the graphs indicated that the intermediate rate-limiting step that dictated the formation of the pyrazines followed a pseudo-first-order kinetic model. As also can be seen from Figures 2 and 3, the reaction time was allowed to be long enough so that there was at least a one log cycle change in the $1 - f$ which is required to accurately identify the reaction order (Lund, 1977). It is important to point out that $[C_0]$ was not necessarily zero since the zero time was taken after 10 min of heating and reactions did occur during the come-up time. In Figures 2 and 3, $1 - f$ was calculated with a $[C_0]$ of 10 ppm and a $[C_\infty]$ of 91.1 ppm for 2,5-dimethylpyrazine and a $[C_0]$ of 1.5 ppm and a $[C_\infty]$ of 20.9 ppm for 2-methylpyrazine.

The pre-exponential constant, $[A_0]$, and the activation energy, E_a, for the formation of 2,5-dimethylpyrazine were determined using a statistical parameter estimation technique based on least-squares fit as follows:

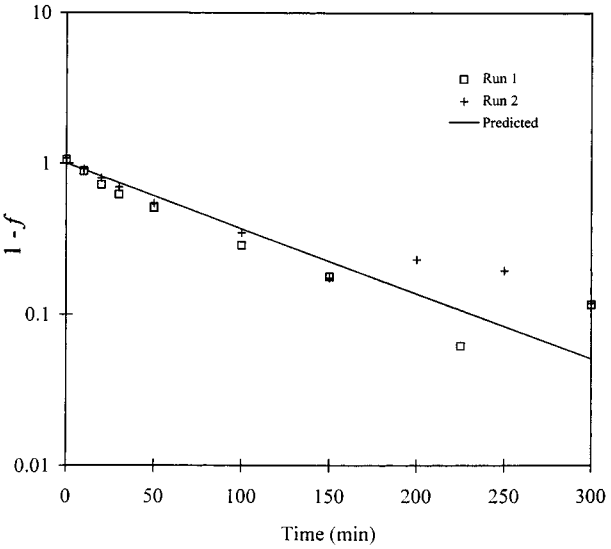

Figure 2. Kinetics of 2,5-dimethylpyrazine formation at 90 °C using the fractional conversion technique.

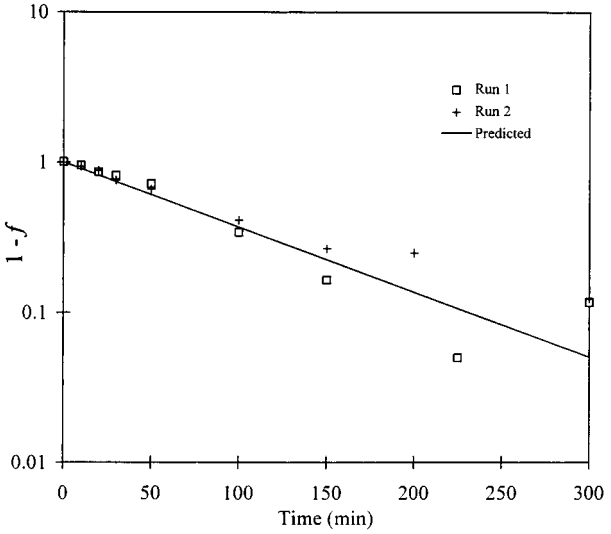

Figure 3. Kinetics of 2-methylpyrazine formation at 90 °C using the fractional conversion technique.

(1) The guessed initial values of $[A_0]$ and E_a were entered into a statistical package and the rate constants from 80 to 120 °C were calculated by eq 17.

(2) The concentration of 2,5-dimethylpyrazine as a function of time at various constant temperatures was calculated by eq 18 by knowing the $[C_0]$ and $[C_\infty]$ as a function of temperature.

(3) The degree of fit was judged by the sum of the squares between the predicted and the experimentally measured concentrations.

(4) Steps 1−3 were reiterated by entering new values of $[A_0]$ and E_a.

(5) $[A_0]$ and E_a for 2,5-dimethylpyrazine were the values that corresponded to the smallest sum of squares.

The equilibrium concentrations ($[C_\infty]$) of 2,5-dimethylpyrazine and 2-methylpyrazine from 80 to 120 °C are shown in Figures 4 and 5, respectively. Although there was no theoretical basis, it was interesting to observe that the $[C_\infty]$ increased linearly with temperature for both pyrazines. The following equations relate the $[C_\infty]$ in ppm to temperature:

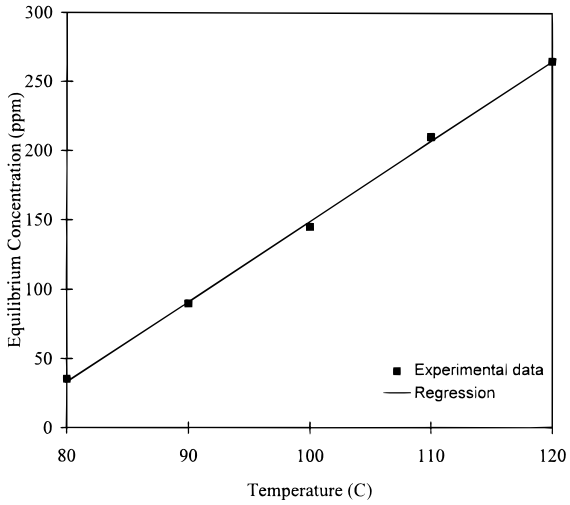

Figure 4. Equilibrium concentration (maximal achievable concentration) of 2,5-dimethylpyrazine as a function of temperature.

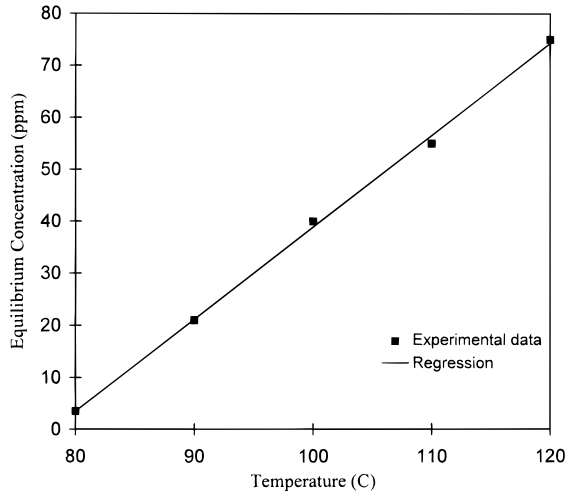

Figure 5. Equilibrium concentration (maximal achievable concentration) of 2-methylpyrazine as a function of temperature.

for 2,5-dimethylpyrazine

$$[C_\infty] = 1.78T - 139.9;\ 80 \le T \le 120\ °C;\ r^2 = 0.999 \quad (20)$$

for 2-methylpyrazine

$$[C_\infty] = 5.80T - 430.5;\ 80 \le T \le 120\ °C;\ r^2 = 0.998 \quad (21)$$

The increase in the equilibrium concentrations of both pyrazines with respect to temperature is consistent with observations made in the literature reporting significantly greater yields of pyrazines at high temperatures and their predominance in roasted foods (Koehler et al., 1971; Maga, 1992; Hwang et al., 1994). Koehler and Odell (1970) postulated two pathways by which alkylpyrazines can be formed from sugar−amine reactions in foods. In the first pathway, the sugar molecules react with amino acids and then condense to form ditetrahydroxybutylpyrazine. This intermediate would rearrange and cleave to form alkylpyrazines. However, at high temperatures the sugars may undergo immediate rearrangements and cleavage to form many small dicarbonyl and hydroxycarbonyl fragments, which can condense with the nitrogen from amino acids to form alkylpyra-

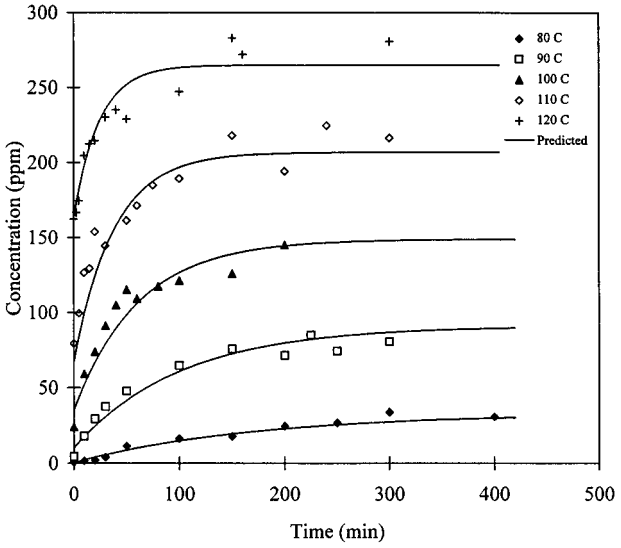

Figure 6. Prediction of 2,5-dimethylpyrazine formation in the solid model system as a function of time and temperature.

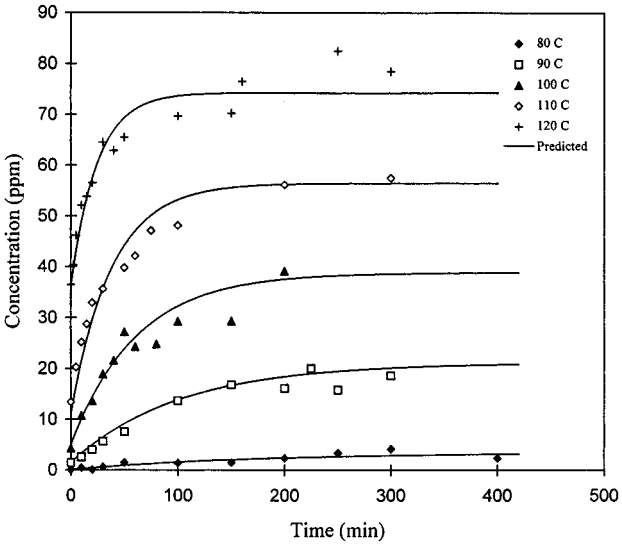

Figure 7. Prediction of 2-methylpyrazine formation in the solid model system as a function of time and temperature.

Table 2. Pseudo-First-Order Rate Constants for 2,5-Dimethylpyrazine Formation in the Solid Model System As Determined Using the Fractional Conversion Technique

temp (°C)	k (min^{-1})	temp (°C)	k (min^{-1})
80	0.00580	110	0.0262
90	0.00986	120	0.0411
100	0.0163		

zines. The authors went further to postulate that the first pathway may be of greater importance at low temperatures and at longer times, while the second pathway may be a more important mechanism at higher temperatures.

The pre-exponential constant and the activation energy for 2,5-dimethylpyrazine were determined to be 1.31×10^6 min^{-1} and 13.5 kcal/mol, respectively. The predicted concentrations of 2,5-dimethylpyrazine as a function of time and temperature using these values and eqs 17, 18, and 20 as well as the experimental data are shown in Figure 6. Each experimental data point was the average of two replicates, with an average standard deviation of ±10%. Although every possible effort was made to reduce the standard deviation between runs, some significant variations were still observed, especially at the higher temperatures and longer reaction times. In general, the agreement between the experimental and the calculated values was quite satisfactory. The concentration of 2,5-dimethylpyrazine over the entire extent of the reaction including the initial period, the change of slope, and the plateau were predicted correctly by the first-order kinetic model with the application of the fractional conversion technique. The rate constants at the different temperatures are given in Table 2.

From the mechanistic standpoint, it is conceivable that pyrazines or a group of pyrazines could be formed by a similar series of reactions (Rizzi, 1972; Shibamoto, 1989) and share the same rate-limiting step. If this is true, two pyrazines should possess the same kinetic parameters. To test this hypothesis, the same activation energy and the pre-exponential constant obtained for 2,5-dimethylpyrazine were utilized to calculate the concentration of 2-methylpyrazine as a function of time and temperature using eqs 17, 18, and 21. The initial concentrations at different temperatures were determined experimentally. As shown in Figure 7, the concentration of 2-methylpyrazine as a function of time was predicted as successfully as that of 2,5-dimethylpyrazine from 80 to 120 °C, indicating that these two compounds indeed shared the same kinetic parameters. Having the same [A_0] and E_a as those of 2,5-dimethylpyrazine for 2-methylpyrazine was further confirmed with the parameter estimation technique outlined previously.

Although the activation energy of 13.5 kcal/mol agreed well with those (13.09−18.84 kcal/mol) reported by Huang et al. (1995) for the formation of tetramethylpyrazine in different solvent systems, it was significantly lower than those determined by Leahy and Reineccius (1989a,b) for 2,5-dimethylpyrazine (41.9−43.7 kcal/mol) and 2-methylpyrazine (34−36.7 kcal/mol) when the rate constants were calculated from the pseudo-zero-order kinetics. The difference was believed to be a result of the difference in the data reduction procedure and the kinetic model used. When the rate constants for the formation of 2,5-dimethylpyrazine and 2-methylpyrazine at different temperatures were determined from the initial slopes of the plots of concentration versus time assuming the reactions would have followed a pseudo-zero-order model, they also fitted reasonably well into the Arrhenius equation for temperature dependence. The calculated activation energies were 36.85 and 43.21 kcal/mol for 2,5-dimethylpyrazine and 2-methylpyrazine, respectively. It is our belief that through the use of the fractional conversion technique, the variability in the activation energy for similar compounds can be significantly reduced or even avoided.

CONCLUSIONS

The following conclusions can be drawn from this study:

(1) The concentrations of 2,5-dimethylpyrazine and 2-methylpyrazine reached a plateau (equilibrium concentrations) in a solid model system when sufficient reaction time was allowed.

(2) The pseudo-zero-order kinetic model failed to predict the concentrations of both pyrazines at prolonged heating times.

(3) A fractional conversion technique was applied to determine the formation kinetics of 2-methylpyrazine and 2,5-dimethylpyrazine.

(4) The formation of 2-methylpyrazine and 2,5-dimethylpyrazine followed a first-order reaction.

(5) The concentrations of 2-methylpyrazine and 2,5-dimethylpyrazine were successfully predicted from 80 to 120 °C, using the same kinetic parameters with an activation energy of 13.5 kcal/mol.

(6) It was believed that the production of 2-methylpyrazine and 2,5-dimethylpyrazine was governed by the same rate-limiting step.

(7) The increase in the equilibrium concentrations with respect to temperature for both pyrazines suggested a shift in chemical pathways that favored greater yields of pyrazines at higher temperatures.

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Received for review October 25, 1996. Revised manuscript received January 24, 1997. Accepted February 13, 1997.[⊗] This is publication D-10126-1-96 and D-10544-8-96 of the New Jersey Agricultural Experiment Station supported by state funds. Financial support from the Center for Advanced Food Technology (CAFT) and the Department of Food Science, Rutgers—The State University of New Jersey is greatly acknowledged. CAFT is a New Jersey Commission on Science and Technology Center.

JF960819P

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.