# Kinetic Analysis of Formation and Degradation of 1-Morpholino-1-deoxy-D-fructose

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The kinetics of the reaction of glucose with morpholine to produce morpholino-1-deoxy-D-fructose (Amadori product) were studied under experimental conditions that minimize side reactions and maximize Amadori product formation (pH 3.0, $T$ = 100 °C, 90% methanol−water, 6 h). Glucose (0.1 M) was reacted in sealed vials with a series of morpholine solutions (0.1−0.3 M), and similarly morpholine (0.1 M) was reacted with different concentrations of glucose (0.05−0.2 M). At specific time intervals, the samples were analyzed for the presence of reactants and Amadori product by a multidetector HPLC system (diode array and pulsed amperometric detector). Under the experimental conditions, morpholine alone (in the presence of glucose equivalent of sorbitol) and glucose alone (in the presence of morpholine equivalent of triethylamine) did not degrade. Similarly, the degradation of Amadori product (0.02 M) was also studied in the presence of excess glucose. The data obtained were used to study the kinetics of color and fluorescence formation and to calculate the rate constants for the formation and degradation of Amadori product using two approaches: one involving the use of integrated rate laws and graphical methods and the second involving simultaneous numerical solutions of the differential rate equations followed by optimization, such that the proposed model fits best the data. Both approaches gave comparable results. The second-order rate constant for the formation of morpholine Amadori compound was calculated to be 1.87 $M^{-1}$ $h^{-1}$.

**Keywords:** *Kinetics; morpholine/glucose; color and fluorescence; graphical and numerical analysis*

## INTRODUCTION

Kinetics of the early Maillard reaction can be divided for convenience into two phases: (1) generation of the Amadori rearrangement product (ARP) (rate of formation) and (2) reactions leading to its destruction (rate of loss). However, the measured concentration of ARP at any time is the concentration of accumulated Amadori product. The factors that complicate the kinetic analysis are the side reactions of amino acid and sugar and the regeneration of amino acid from the Amadori product. Thus, the rate of loss of either sugar or amino acid does not necessarily indicate the rate of formation of ARP. However regeneration of the amine permits the differentiation between two reaction pathways: one in which the C−N bond of the Amadori product is cleaved and the other in which it remains intact. General kinetic models have been proposed for the Maillard reaction by Debrauwer et al. (1991), Vernin et al. (1992), Baisier and Labuza (1992), and Yaylayan and Forage (1992). Most of these models agree with a general scheme in which the reducing sugar (S) reacts with the amine (A) to produce a Schiff base which undergoes the Amadori rearrangement to produce the Amadori product (ARP), which itself degrades to a set of reactive compounds and free amines that recycle (see Scheme 1). In addition, the sugar may react with the Amadori product to produce diglycated Amadori products (diARP). These reactive intermediates then further react to produce fluorescent compounds and brown polymers.

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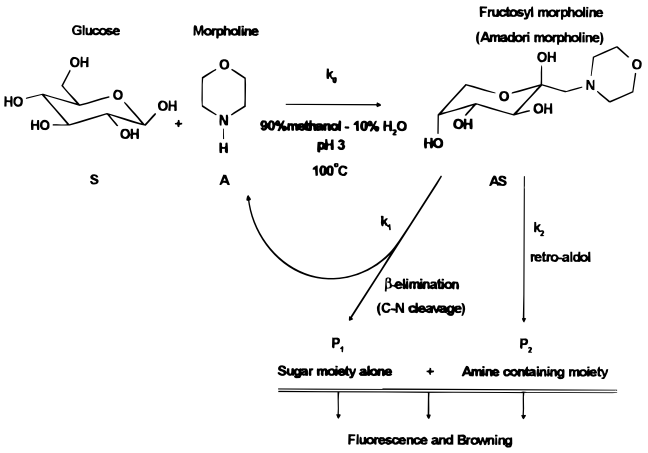
**Scheme 1. Kinetic Model for the Formation and Decomposition of Amadori Morpholine**




The second-order rate equation for the formation of ARP can be written as shown below:

$$\frac{d[ARP]}{dt} = k_o[S][A]$$

However, the observed or measured rate of the formation of ARP (which will be referred to as the rate of accumulation) is given by the rate law

$$\text{rate of accumulation} = \frac{d[ARP]}{dt} = k_o[S][A] - k_1[ARP] - k_2[ARP] - \cdots - k_n[ARP]$$

where $k_1$, $k_2$, and $k_n$ are the rate constants for different decomposition reactions of Amadori product. Generally,

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the rate constants of reactions that follow second-order kinetics of the type shown below depend on the initial concentrations of the reactants, and the first-order rate loss of each reactant will increase when the concentration of the second reactant is increased.

$$\frac{d[X]}{dt} = k[A][B]$$

This has been observed at 37 °C in the reaction of glycine with glucose (Baisier and Labuza, 1992). However, at 60 °C, Vernin et al. (1992), using computer-simulated kinetic analysis of data obtained from the reaction of glucose with three different amino acids, have observed that irrespective of the initial ratio of the reactants the observed rate of glucose disappearance was always faster than that of the amino acids (except proline); if these results can be trusted, it may mean glucose is undergoing other side reactions (such as forming diglycated products and amino acid-catalyzed decompositions) more extensively than amino acids and that the rate of amino acid release from Amadori product is not negligible. In addition, the rate of sugar loss was also dependent on the type of amino acid: Glucose disappeared 10 times slower in the presence of proline than in the presence of valine or methionine (Debrauwer et al., 1991; Vernin et al., 1992).

## MATERIALS AND METHODS

All reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI). HPLC solvents were filtered and degassed (ultrasound/vacuum) prior to usage. The Amadori compound of morpholine was purchased from Sigma Chemical Co. (St. Louis, MO). The statistical analysis was performed with the Mathematica software for Windows (ver. 2.1) of Wolfram Research Inc. (Champaign, IL). For programming examples in Mathematica, see the Supporting Information.

**Kinetic Runs.** D-Glucose (0.05−0.2 M, final concentrations) and morpholine (0.1−0.3 M, final concentrations) solutions (pH ≅ 3, adjusted with phosphoric acid, as determined in a 100% aqueous mixture at room temperature) in 90% methanol/water (1:1−1:3 relative ratios) were incubated in sealed tubes at 100 °C for 6 h. The progress of the reaction was monitored at specific time intervals. Degradation of glucose by itself was performed in the presence of triethylamine, and that of morpholine was performed in the presence of sorbitol (both solutions were at pH ≅ 3, adjusted with phosphoric acid). The results represent the average of duplicate analyses.

**HPLC Analysis.** Concentrations were determined by a multidetector HPLC system (Huyghues-Despointes and Yaylayan, 1994). Glucose was measured by pulsed amperometric detection (PAD) at a gold electrode (Hewlett Packard, model 1049A). Morpholine and Amadori morpholine were measured by a diode array detector (Beckman System Gold, module 168), set to monitor the region between 190 and 460 nm. The carbohydrate-dedicated column of Waters (10 mm, 4.6 mm × 30 cm; later the guard column was purchased from Waters, Bondapak NH2 WAT046865) was used. The guard column consisted of the Brownlee aminopropyl cartridge (Amino Spheri-10, 3 cm × 4.6 mm). The mobile phase consisted of 70% acetonitrile and 30% phosphate buffer (0.004 M, pH 7.0). The flow rate was set at 1 mL/min.

**Measurement of Fluorescence and Color.** Color differences were calculated from measured Hunter tristimulus data, using a Chroma Meter model CT-210 colorimeter. Fluorescence formation was followed by a fluorescence detector (Shimadzu, model RF-551), at excitation/emission wavelengths of 350/420 nm.

## RESULTS AND DISCUSSION

The mechanism of formation of ARP by the reaction of reducing sugars with amino acids and its subsequent decomposition is a complex process which depends primarily on the reaction conditions such as temperature, pH, time, water content, and the relative ratio of the reactants and their concentrations. In the context of the kinetic analysis, certain assumptions should be made regarding the mechanism in order to simplify the mathematical calculations. The assumption that sugar and amino acid alone do not undergo decomposition in our model system consisting of glucose and morpholine holds true under the experimental conditions as verified by heating these reactants separately. Furthermore, these acidic conditions ensure that the amine is mostly in its protonated form. This consideration is of importance since to observe true second-order kinetics, the concentration of the reactants, the unprotonated amine, and the open chain form of glucose should be of the same order of magnitude. Morpholine is a secondary amine, whereas the resulting Amadori product is a nonreactive tertiary amine. In addition, the lack of a carboxylic acid group will minimize side reactions, such as decarboxylation and Strecker degradation. The general kinetic model for the reaction of glucose with morpholine, as proposed in Scheme 1, stipulates the formation of the Amadori product with a second-order rate constant of $k_o$ and subsequent decompositions by two pathways: one initiated by C−N bond cleavage to regenerate the amine with a rate constant of $k_1$ and the other without C−N bond cleavage with a rate constant of $k_2$.

Glucose was reacted in sealed vials, with a series of morpholine solutions, and similarly, morpholine was reacted with different concentrations of glucose. At specific time intervals, the samples were analyzed for the presence of reactants and Amadori product by the multidetector HPLC system (diode array and pulsed amperometric detector). Two approaches were used for the determination of the reaction kinetics. The first involves the use of integrated rate laws and graphical methods, whereas the second method involves simultaneous numerical solutions of the differential rate equations and optimization such that the proposed model fits best the data. Preliminary results obtained using the graphical method were presented earlier (Huyghues-Despointes and Yaylayan, 1995).

**Integrated Rate Laws and Graphical Methods.** *Glucose−Morpholine Reaction Kinetics.* To calculate the rate constants $k_o$, $k_1$, and $k_2$, it was assumed that at any time $t = t_1$, $x$ mol of sugar react with $x$ mol of amine to produce $x$ mol of Amadori product (AS). A certain fraction of AS ($rx$ mol) decomposes to regenerate the amine, and $r'x$ mol decomposes through other pathways ($0 < r$ and $r' < 1$); therefore

at $t = t_1$, $S = (S_o - x)$

$$A = (A_o - x + rx) \qquad AS = (x - rx - r'x)$$

where $S$, $A$, and $AS$ are the measured concentrations of sugar, amine, and the Amadori product, respectively. By solving simultaneously the above three equations with three unknowns, the following values for $x$, $r$, and $r'$ can be obtained with either known or experimentally measured values:

$x = S_o - S$,

$$r = A_o - A + S - S_o/(S - S_o)$$

$$r' = 1 - r - [AS/(S_o - S)]$$

where $S_o$ and $A_o$ are the initial concentrations of sugar and amine, respectively.

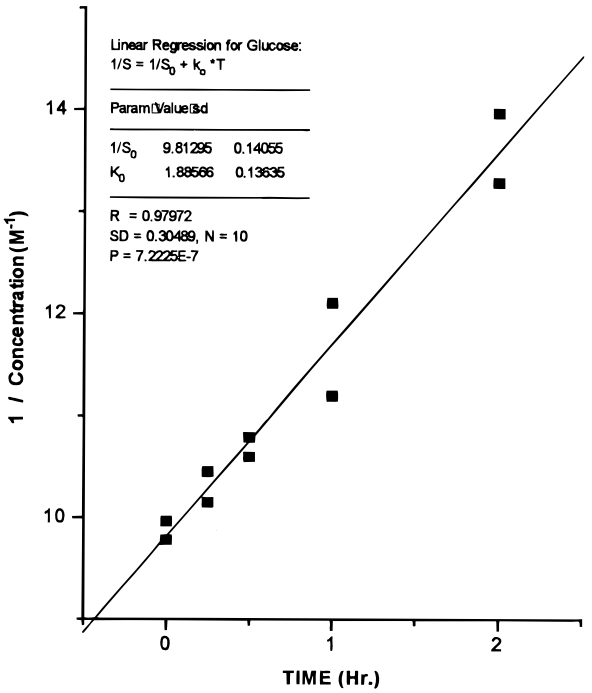



**Figure 1.** Plot of $1/S$ vs time for model system of glucose: morpholine (1:1 molar ratio).

Knowledge of the fraction of Amadori product undergoing C−N cleavage ($rx$) and other fragmentations ($r'x$) under specific conditions allows the evaluation of their relative importance and contribution to the overall aroma profile. Such analysis can eventually lead to controlled production of Maillard reaction mixtures, enriched with specific types of products for flavor application purposes such as reaction flavors.

Under the experimental conditions, the absolute value of the rate of loss of sugar is equal to the rate of formation of Amadori compound, and the differential rate law for the second-order reaction is given by the following equation:

$$\frac{\mathrm{d}[x]}{\mathrm{d}t} = -k_o[S_o - x][A_o - x]$$

Solving the above equation will generate the rate law for second-order reactions as shown below:

$$\frac{1}{S} = \frac{1}{S_o} + k_o t$$

If the reaction is indeed second order, then plotting $1/S$ vs $t$ will be a straight line with a slope of $k_o$ and an intercept of $1/S_o$. Figure 1 shows the plot of $1/S$ vs $t$ for the sugar/amine ratio of 1:1.

Table 1 also lists the initial rates for other model systems in which the ratio of reactants is not 1:1, calculated using the following equation (Castellan, 1973):

$$\frac{1}{b - ra}\left\{\ln\left(\frac{a}{a - x}\right) - \ln\left[\frac{(b/r)}{(b/r) - x}\right]\right\} = kt,\ r \neq 1$$

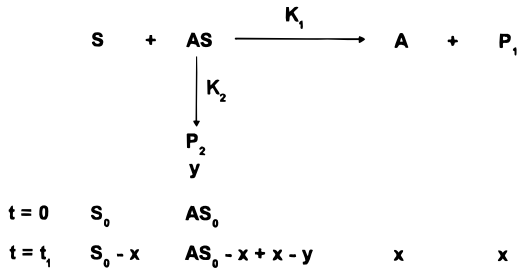
where $r$ is the ratio of reactants, $a$ and $b$ are the initial concentrations of the reactants, and $x$ is the number of mol/L of reactant which reacted at time $t$. The data obtained indicate that the reaction of glucose with morpholine to form the Amadori product follows second-order kinetics and that the highest amount of Amadori product was accumulated when the starting amine concentration was 3 times in excess to that of glucose. A more detailed statistical analysis of the data is presented below.

**Table 1. Calculated Rate Constants[a]**

| | $k_o$ ($M^{-1}$ $h^{-1}$) | | $k_1$ ($h^{-1}$) | | $k_2$ ($h^{-1}$) | |
|---|---|---|---|---|---|---|
| kinetic runs | G | N | G | N | G | N |
| system | | | | | | |
| 3A:1S | 1.45 | 2.25 | 0.48 | 0.37 | 0.37 | 0.08 |
| 1A:2S | 0.96 | 2.07 | 0.49 | 0.30 | 0.22 | 0.26 |
| 1A:1S | 2.10 | 1.94 | 0.28 | 0.25 | 0.26 | 0.29 |
| 1A:0.5S | 0.68 | 2.32 | 0.03 | 0.09 | 0.30 | 0.40 |
| 2A:1S | 1.56 | 1.39 | 0.29 | 0.27 | 0.02 | 0.16 |
| 5S:1SA | nd | nd | 0.35 | nd | 0.32 | nd |
| mean | 1.35 | 1.99 | 0.32 | 0.26 | 0.25 | 0.24 |
| optimized values (overall) | | 1.87 | | 0.26 | | 0.19 |

[a] S = glucose; A = morpholine; AS = Amadori product; nd = not determined; G = graphical method; N = numerical method.

**Scheme 2. Amadori Morpholine Decomposition: Calculation of $k_1$ and $k_2$**




*Kinetics of Decomposition of Morpholine Amadori Compound.* To calculate $k_1$ and $k_2$, the rate constants for the different decomposition pathways of the Amadori product, the decomposition of the morpholino-D-fructose (final concentration of 0.02 M) was studied in 5 molar excess of glucose (final concentration of 0.1 M), under the same reaction conditions as the glucose− morpholine reaction. Assuming that at any time $t = t_1$, $x$ mol of the Amadori product decomposes through C−N bond cleavage and $y$ mol through other pathways, then the values for $x$ and $y$ can be calculated as shown in Scheme 2. During the reaction of Amadori product in the presence of excess glucose, the concentration of the sugar diminished, indicating a reaction with the amine, since it has been established that sugar alone, under the experimental conditions, does not decompose and that the Amadori product being a tertiary amine cannot react with the sugar. However, the concentrations of the amine produced through C−N cleavage were below the detection limit of the system, indicating that in the presence of excess sugar the released amine reacted quickly with the sugar to form Amadori product. Hence, the measured concentration of the sugar ($S$) and the measured Amadori concentration ($AS$) are given by the following equations:

$$S = S_o - x \qquad AS = AS_o - x + x - y$$

Rearranging these equations will yield the values for $x = S_o - S$ and for $y = AS_o - AS$, where $S_o$ and $AS_o$ are the initial sugar and Amadori concentrations, respectively.

For a first-order decomposition of Amadori product, plotting $\ln[(AS_o - x)/AS_o]$ vs $t$ should generate a straight line with a slope of $k_1$; similarly plotting $\ln[(AS_o - y)/AS_o]$ vs $t$ should generate a straight line with a slope of

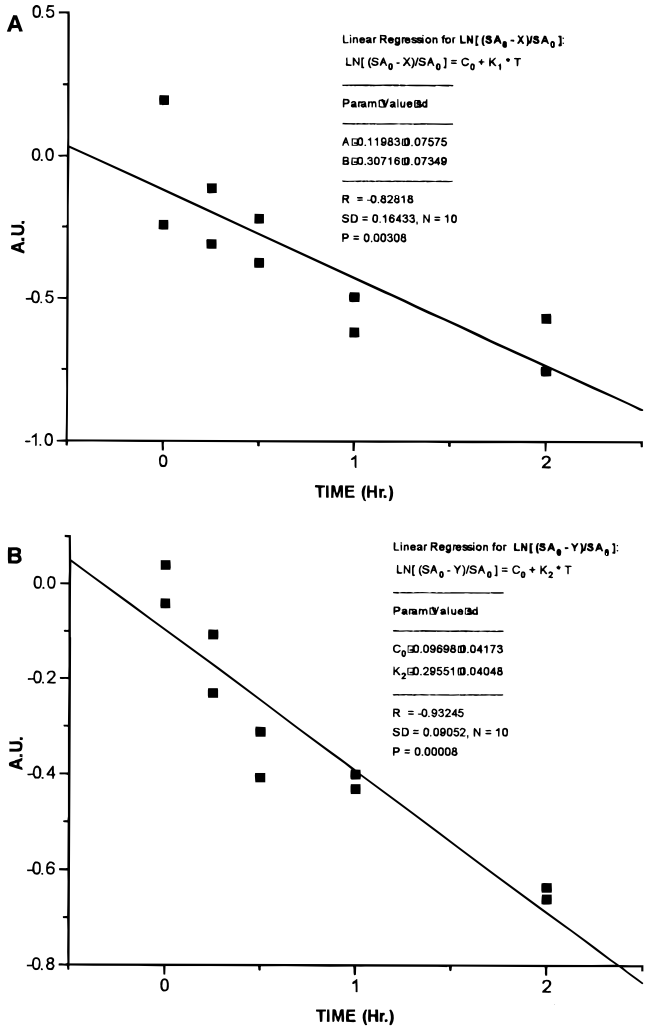



**Figure 2.** Plots of (A) $\ln[(AS_o - x)/AS_o]$ and (B) $\ln[(AS_o - y)/AS_o]$ vs time for Amadori morpholine:glucose model system.

$k_2$. Figure 2 shows the above plots during the initial 2 h period. These plots deviate slightly from linearity at the later stages of the reaction due to the regeneration of the Amadori product by the reaction of the liberated amine and the excess sugar. The calculated values for the decomposition rate constants ($k_1$ and $k_2$) from these plots are listed in Table 1.

**Numerical Evaluations and Optimization.** *Glucose−Morpholine Reaction Kinetics.* The model depicted in Scheme 3 can be described by the rate equations shown below:

$$d[S]/dt = -k_o[S][A]$$

$$d[A]/dt = -k_o[S][A] + k_1[AS]$$

$$d[AS]/dt = -k_o[S][A] - k_1[AS] - k_2[AS]$$

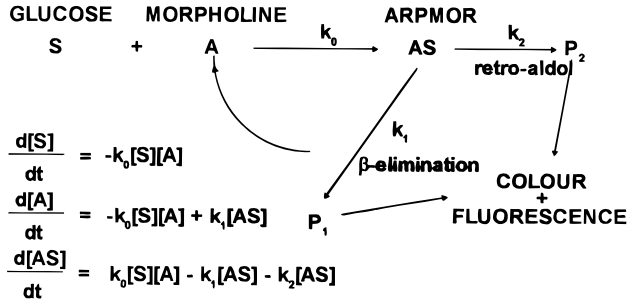
Once the values of $k_1$ and $k_2$ are known, it becomes possible to find the rate of formation of the hypothetical products $P_1$ and $P_2$ by solving the following differential equations:

$$d[P_1]/dt = k_1[AS]$$

$$d[P_2]/dt = k_2[AS]$$

The three unknowns $k_o$, $k_1$, and $k_2$ can be calculated by an optimization procedure where preselected values

**Scheme 3. Differential Equations That Define the Kinetic Model**




for the above unknowns are varied within a predetermined range (boundary conditions) each time the three differential equations (shown in Scheme 3) are solved simultaneously by a Euler based numerical method (NSolve of MATHEMATICA). The concentrations estimated for times $t = 0$, 0.25, 0.5, 1, 2, 3, 4, 5, and 6 h are then compared with the actual experimental values found at the same time intervals. Because of the inherent random errors, it was found best to estimate the concentration at time $t = 0$ for glucose and morpholine by fitting an exponential decay curve to the original data points (best fitted curve chi-square test criterion) and use the predicted value at time zero instead of the simple average of the experimental data at time zero. For comparison purposes, the actual values were subtracted from the calculated values and the difference was squared. The squared differences were added up and are referred to as residual sum of squares. The residual sum of squares (RSS) were calculated for every given value of $k_o$, $k_1$, and $k_2$, for each kinetic run (experiments done with different initial concentrations of sugar and amine) and for all the runs together, essentially creating a four-dimensional space with three independent variables ($k_o$, $k_1$, $k_2$) and one dependent variable (RSS). Then, the best coefficients are estimated according to the least-squares method for the following model which was found to account for at least 95% of all variations:

$$\mathrm{RSS} = \beta_0 k_o + \beta_1 k_1 + \beta_2 k_2 + \beta_{00} k_o^2 + \beta_{11} k_1^2 + \beta_{22} k_2^2 + \beta_{111} k_1^3 + \beta_{222} k_2^3 + \beta_{01}(k_o k_1) + \beta_{012}(k_o k_1 k_2) + \epsilon$$

Best fit equation:

$$\mathrm{RSS} = 0.0876698 - 0.0528059 k_o + 0.017113 k_o^2 - 0.165576 k_1 - 0.0439445 k_o * k_1 + 0.693379 k_1^2 - 0.580747 k_1^3 - 0.0958182 k_2 - 0.299704 k_2^3 + 0.00826978 k_o * k_1 * k_2 + 0.327452 k_2^2$$

Once the best fitted equation is found, the method of steepest descent (FindMinimum in MATHEMATICA) is used to evaluate the minimum (the use of different starting points always resulted in the same minimum). The minimum is found at specific $k_o$, $k_1$, and $k_2$ values. With these values, it is now possible to compare the calculated concentrations with the observed concentrations and evaluate the goodness of fit of the model by regressing the observed concentrations on the concentrations calculated from the model with the optimized $k_o$, $k_1$, and $k_2$ values. The regression statistics (for details, see the Supporting Information) not only show

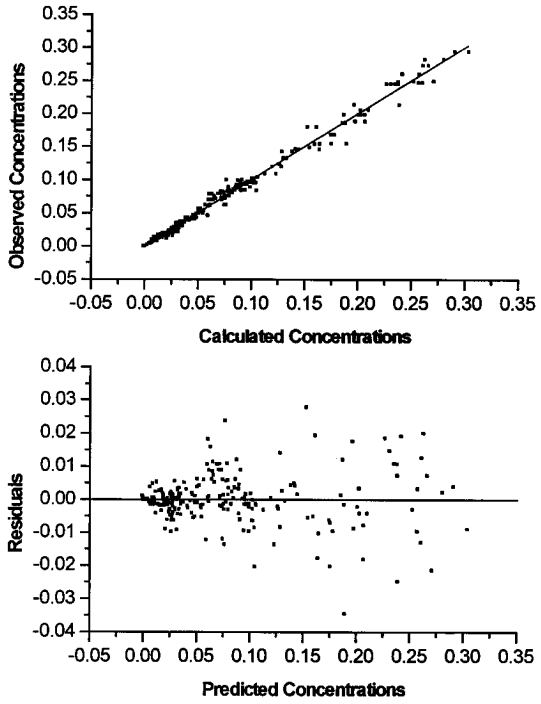



**Figure 3.** Predicted versus observed concentrations for the optimized model.

a very high correlation coefficient but also a theoretical slope of 1, which indicates that the model fits the data quite well. This is also illustrated in Figure 3. Although the residuals are fairly randomly distributed, they increase at higher concentrations, an indication that weighted regression might have been favorable.

To further decompose the residuals, these were plotted against time for each of the components: the sugar, the amine, and the Amadori product. According to these plots, the residuals are randomly distributed with time when the three products are taken together. However upon decomposition of the residuals into the individual contributions by the sugar, amine, and the Amadori product, the data show that the absolute values are higher in the case of the amine. This could be a direct consequence of the chromatographic problems associated with the interaction of amines with silica-based columns. (Using the Brownlee guard column resulted in extensive retention of the morpholine. Interestingly, the use of a guard column purchased from Waters not only decreased significantly the retention time but also improved substantially the associated peak symmetry.) Another point that becomes apparent is that the residuals associated with ARP might not be randomly distributed. Initially, because the concentration of ARP increases relatively fast, the errors associated with the analysis and detection are larger. From 5 h and on, there is an indication that the model might not hold true. Figure 4 illustrates the observed and calculated concentrations as they vary with time for glucose/morpholine mixtures. Figure 4 again shows that the deviations become more pronounced from 5 h and on. Actually, the fact that the model fits the data up to 4 h at 100 °C is quite surprising, taking into account the complexity of the overall chemistry involved. It appears that the model, from 5 h and on, overestimates the decomposition of ARP. This can be explained by an overestimation of the amount of morpholine regenerated from the ARP. As the decomposition of ARP progresses, sufficient product(s) arising from the $k_2$ pathway accumulate and may themselves degrade and regenerate

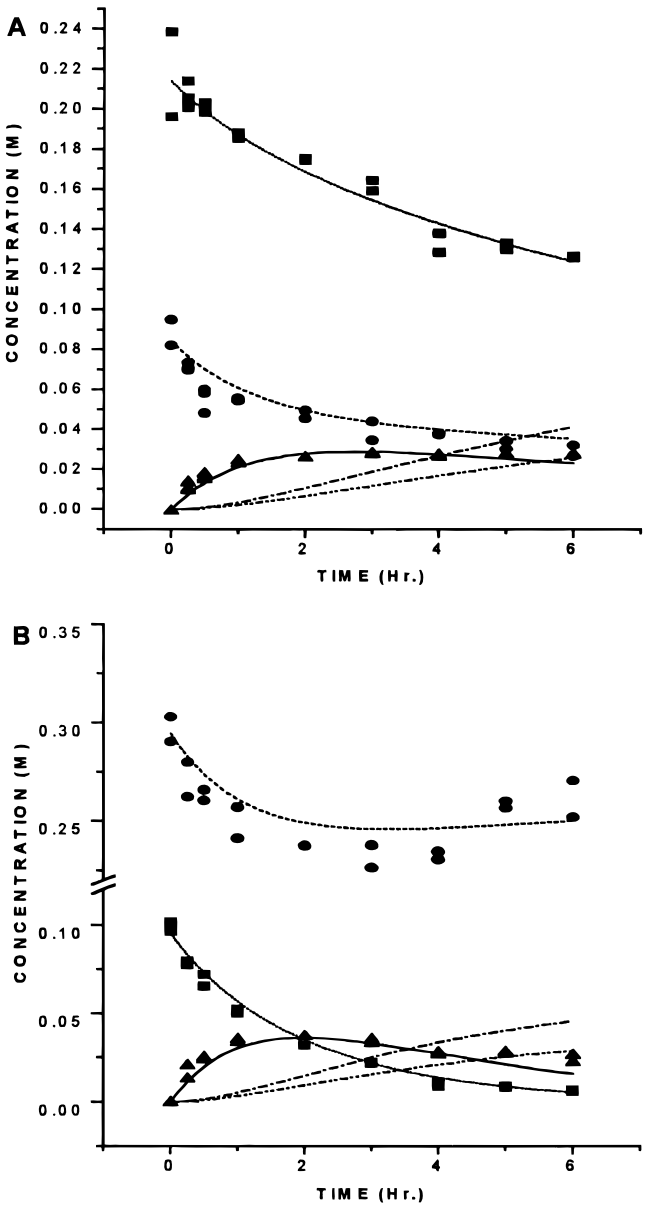



**Figure 4.** Plots of the calculated concentrations (lines) and observed concentrations (points) vs time: (A) glucose = 0.2 M and morpholine = 0.1 M, (B) glucose = 0.1 M and morpholine = 0.3 M; glucose concentrations observed (■) and calculated (···); morpholine concentrations observed (●) and calculated (– – –); Amadori morpholine concentrations observed (▲) and calculated (—); estimated concentrations of $P_1$ (—·—) and $P_2$ (—··—).

the amine. As a validation for the model, ARP was decomposed in the presence of glucose without initial addition of morpholine and the calculated values were compared with the observed concentrations. This kinetic run was not included in the optimization step. Using the optimized values for $k_o$, $k_1$, and $k_2$, to calculate the theoretical concentrations as a function of time resulted in a fairly good agreement with the observed concentrations. Table 1 compares the values of $k_o$, $k_1$, and $k_2$ obtained by both graphical and numerical methods.

**Chemical Interpretation.** The data obtained indicate that the reaction of glucose with morpholine to form Amadori product follows second-order kinetics. According to this model, the rate of formation of ARP increases as the concentration of the starting sugar or amine increases, as expected for a bimolecular reaction. However, the concentration of ARP attains a quasi

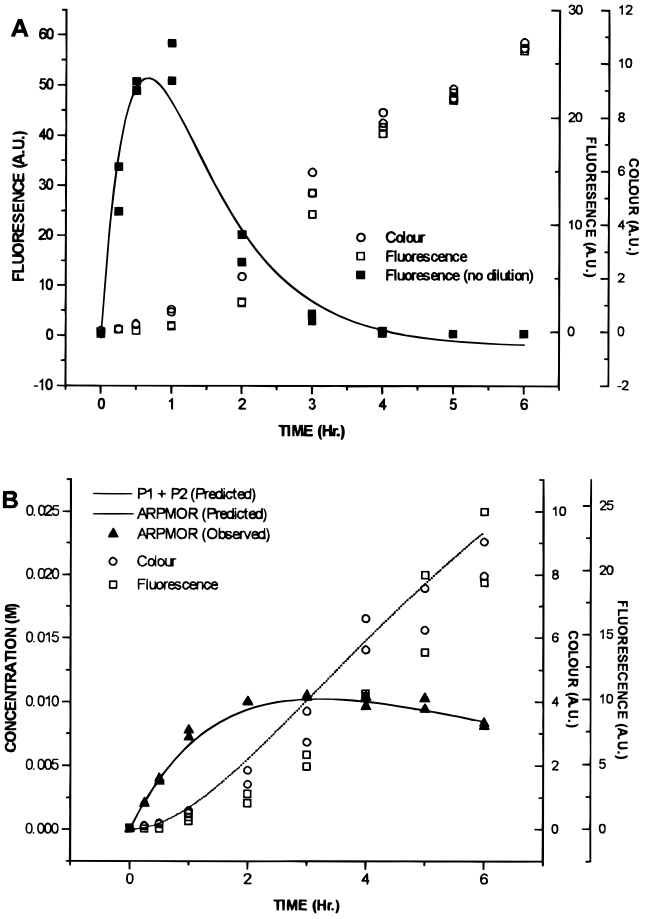



**Figure 5.** Kinetics of fluorescence and browning (color): (A) time relationship of fluorescence prior and after dilution relative to browning and (B) relationship of Amadori morpholine degradation and the appearance of fluorescence and browning.

steady state, as long as there is excess sugar present in the mixture to react with the regenerated amine (Figure 4A). In the case of a high amine concentration relative to that of sugar (Figure 4B, ratio 1:3), although the rate of formation of ARP and its overall concentration might be high, its apparent rate of decomposition is also fast due to the disappearance of sugar from the solution which prevents the attainment of a quasi steady state.

The kinetic analysis shows clearly, in the case of secondary amines under dehydrating conditions and at low pH values, that the major source of flavors and colors is the degradation of the Amadori products (a lower energy pathway) and that the reactions of Amadori products proceeding by either carbon−nitrogen bond cleavage ($k_1$) or without cleavage ($k_2$) are equally important degradation pathways.

**Kinetics of Color and Fluorescence Formation.** In addition to monitoring the concentrations of different reactants and products, color and fluorescence were also measured as a function of time. Figure 5 shows the results obtained. Analysis of the data shows that fluorescence follows a bell-shaped curve prior to proper dilution, due to the formation of strong fluorescence-quenching compounds (Figure 5A). However, upon 1:100 dilution in water, it was found that the kinetics of fluorescence formation was very similar to that of brown color formation, contrary to the published literature (Labuza and Baisier, 1992), which indicates that fluorescent species are the precursors of brown polymers. As shown in Figure 5, the rate of color and fluorescence formation follows fairly well the predicted rate (by the kinetic model) of formation of Amadori morpholine degradation products ($P_1 + P_2$) but with a slight time lag, indicating that $P_1$ and $P_2$ must further react to produce color and fluorescent materials. Overall, these results indicate that the model fits well the data and that the decomposition of the Amadori product eventually leads to simultaneous color and fluorescence formation.

**Conclusion.** The kinetic data indicate that the reaction of morpholine with glucose to form the Amadori product follows second-order kinetics and that the decomposition pathway of the resulting Amadori compound is not only dictated by carbon−nitrogen bond cleavage reactions but also by reactions initiated by the intact Amadori compound.

**Supporting Information Available:** Programming examples and regression statistics (10 pages). Ordering information is given on any current masthead page.

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