Nonenzymatic Browning Behavior, As Related to Glass Transition, of a Food Model at Chilling Temperatures[†]

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A food model composed of maltodextrin, lysine, and xylose was developed to study nonenzymatic browning at low temperatures (5, 10, and 20 °C) around the glass transition temperature (T_g) region of the matrix. The extent of nonenzymatic browning at various $T - T_g$ conditions was followed spectrophotometrically at 420 nm. Nonenzymatic browning occurred at low temperatures and intermediate water contents, showing an increasing rate with increasing water content. The rate of the reaction at each water content increased with increasing temperature. The rate was extremely low below T_g, probably because of limited diffusion. The browning reaction in a suitable matrix can be used to indicate the time–temperature history of chilled foods.

INTRODUCTION

Nonenzymatic browning (Maillard reaction) is one of the most important chemical phenomena that may affect food quality in processing and storage. It may contribute to food palatability by improving flavor and color. However, in dehydrated foods, browning results in deterioration, mainly by producing off-flavors and off-colors, and it may cause loss of nutritional value [e.g., Hodge (1953), Namiki (1988), Labuza and Baisier (1992)]. Nonenzymatic browning is an amino–carbonyl reaction. Its mechanism and kinetics in real foods and in models, containing reducing sugars and amino compounds as reactants, have been studied intensively. These studies have revealed the various stages of the nonenzymatic browning reaction and shown that the rate of the reaction is strongly dependent on material composition, temperature, moisture content, and pH [e.g., Hodge (1953), Karel and Nickerson (1964), Labuza et al. (1970), Labuza (1980), Labuza and Saltmarch (1981), Petriella et al. (1985), Buera et al. (1987), Labuza and Baisier (1992)].

The nonenzymatic browning reaction has been usually considered to follow zero-order kinetics, after an initial induction period, and the temperature dependence has been modeled with the Arrhenius equation [e.g., Mizrahi et al. (1970a,b), Labuza (1980), Labuza and Saltmarch (1981), Samaniego-Esguerra et al. (1991), Baisier and Labuza (1992)]. The reaction rate at intermediate water contents, with a corresponding product equilibrium relative water vapor pressure or water activity (a_w) below 90% or 0.9, respectively, has been shown to be strongly moisture-dependent. Labuza et al. (1970) reported that dehydrated foods have a slow browning rate at low water activities. The maximum browning rate occurred at the a_w range typical of intermediate-moisture foods. It was proposed that at low water contents the reaction is controlled by diffusion of the reactants. At water contents above that for maximum browning, the rate of the reaction decreases due to dilution of the water-soluble reactants. However, at low water contents, an increased reaction rate may result from the plasticization of the material with plasticizers such as glycerol (Eichner and Karel, 1972), and at high water contents, the moisture dependence becomes negligible (Petriella et al., 1985).

Removal of water from biological materials often results in the formation of an amorphous continuous matrix. This matrix may exist as a highly viscous glass or as an elastic "rubber" [e.g., White and Cakebread (1966), Slade and Levine (1991), Roos and Karel (1991a)]. The physical stability of amorphous materials can be characterized in terms of glass transition temperature (T_g). Below T_g, molecules have very low mobility and they are "frozen" in the highly viscous, nonequilibrium, solid-like, glassy state [e.g., Tant and Wilkes (1981), Slade and Levine (1991)]. Above T_g, the viscosity of the material decreases exponentially with increasing temperature, due to thermal plasticization. Amorphous biological and food materials are also significantly plasticized by water, and even small amounts of adsorbed water may cause a dramatic decrease of T_g (Slade and Levine, 1991). The physical state of dehydrated food materials has been suggested to be one of the rate-defining factors of diffusion-controlled deteriorative changes, including nonenzymatic browning, in low- and intermediate-moisture foods (Eichner and Karel, 1972; Slade and Levine, 1991; Roos and Karel, 1991a; Karmas et al., 1992). In these studies, the rate of browning has been considered to be controlled by diffusion of the reactants. Above T_g, increasing diffusion may be related to decreasing viscosity, and instead of using the Arrhenius-type temperature dependence of the reaction rate, the use of an alternative Williams–Landel–Ferry model (WLF; Williams et al., 1955) has been suggested (Slade and Levine, 1991; Karmas et al., 1992; Buera and Karel, 1993).

Karmas et al. (1992) concluded that the rate of browning of several vegetables and food models is very slow below T_g, but at temperatures above T_g, in addition to the decreasing viscosity, other changes such as crystallization and collapse affect the browning rate. Although the rate of browning has been found to be affected by the physical state, the temperature dependence of experimental browning rates in the T_g range has followed both the Arrhenius and WLF models (Karmas et al., 1992; Nelson and Labuza, 1992). In addition, most of the kinetic data for the nonenzymatic browning reaction at various water contents have been determined at temperatures above 25 °C, and there have been no studies reporting browning rates at low temperatures. In this study, a noncrystallizing food model was developed to determine the browning rate as a function of water content, water activity, and glass transition temperature. The results were used to establish relationships between the nonenzymatic browning rate,

temperature, and physical state of the model. Since the nonenzymatic browning rate may be comparable with the rate of food deterioration, we also evaluated the suitability of the extent of the color formation to indicate quality loss of chilled foods.

MATERIALS AND METHODS

Food Model Preparation. A commercial maltodextrin (Maltrin M100, Grain Processing Corp., Muscatine, IA) was used as the main component of the food model. Maltodextrins (starch hydrolysis products) are composed of a wide range of glucose polymers (Brooks and Griffin, 1987). They may increase the recrystallization rate of starch at high water contents (Biliaderis and Zawistowski, 1990), but in low-moisture sugar mixtures, they delay crystallization (Labrousse et al., 1992). Loss of adsorbed moisture has not been observed in sorption isotherms as would be expected if crystallization had occurred (Roos, 1993a). Therefore, we considered maltodextrins as noncrystallizing materials at low water contents. A noncrystallizing food model was important, since crystallization of lactose in milk powders has been found to increase the rate of nonenzymatic browning (Saltmarch et al., 1981). Such crystallization of amorphous food components may occur above T_g (Roos and Karel, 1992).

A 20% (w/w solids) clear solution was prepared from the maltodextrin, L-lysine (3.5% of total solids; Fluka), D-xylose (3.5% of total solids; Merck), and distilled water at room temperature. Lysine and xylose were used because of their high reactivity (Karmas et al., 1992). The amount of the reactants was adjusted by observing color formation at low temperatures, and their concentration was kept as low as possible to keep the possible decrease of reaction rate due to decreasing reactant diffusion observable (Karmas et al., 1992). The maltodextrin used had a low dextrose equivalent value (DE) of 10, and its effect on the browning reaction was considered negligible. The solution was frozen (5-12 h at -20 °C), immediately after preparation on Petri dishes in 15-17-mL aliquots, and freeze-dried (18-20 h; Edwards EF 10/10, $p < 0.1$ mbar) to produce a completely amorphous glassy state of the food model (Roos and Karel, 1991a). The dried material was further dehydrated and stored over P_2O_5 at room temperature. No color formation was observed in the "anhydrous" samples.

Water Adsorption. Amorphous maltodextrins are significantly plasticized by water (Roos and Karel, 1991a; Slade and Levine, 1991). Thus, critical water contents or water activities, above which they exist as rubbers at room temperature, can be established (Roos, 1993a). We determined the water adsorption of the food model at 23 °C gravimetrically as an average of six measurements. The material was powdered and prepared in differential scanning calorimeter (DSC) pans (Mettler 40-µL aluminum pans). The samples (4-10 mg) were rehumidified for at least 1 week in vacuum desiccators with various relative humidities (RH), as reported by Roos and Karel (1991a). Various saturated salt solutions [LiCl, CH₃COOK, MgCl₂, K₂CO₃, Mg-(NO₃)₂, CoCl₂, NaCl, and KCl] were used to achieve RH values of 11.6, 24.1, 33.1, 44.5, 54.0, 66.0, 76.6, and 86.2%, respectively (Greenspan, 1977; Labuza et al., 1985). The rehumidified samples were hermetically sealed in the DSC pans and weighed using an analytical balance (Mettler AT20). The water adsorption data were modeled using the BET and GAB sorption isotherm models, as reported by Roos (1993a).

Glass Transition Temperature. The glass transition temperature of the food model, at various water contents (m) and a_w values $(0.01 \times \%$ RH at equilibrium), was determined using differential scanning calorimetry. The instrument (Mettler TA4000 system with TC10A processor, DSC 30 measuring cell, and GraphWare TA72AT.2 software) was calibrated using n-hexane, distilled water, and indium, as reported by Roos and Karel (1991b). The samples with known m and a_w values, hermetically sealed in the DSC pans in the water adsorption study, were cooled to at least 30 °C below T_g and scanned, at 5 °C/min, to at least 30 °C above the endset of the glass transition temperature range (Roos, 1993b). The T_g values reported are *onset* temperatures of the glass transition temperature range (Roos and Karel, 1991b). T_g values and water contents were also determined for samples, stored at 5, 10, and 20 °C in vacuum
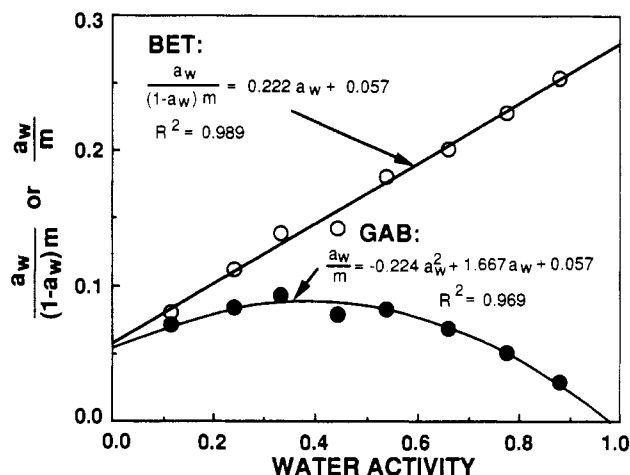

Figure 1. Calculation of the BET and GAB isotherm models, with the experimental adsorption data using linear regression analysis.

desiccators over saturated Mg(NO₃)₂, CoCl₂, NaCl, and KCl solutions, after 1 and 3 weeks of storage. These T_g values were used in the analysis of the nonenzymatic browning rate at various $T - T_g$ conditions. Determination of T_g after different storage times also confirmed that the samples remained amorphous, with a constant $T - T_g$ value, during color formation and storage.

Nonenzymatic Browning. Samples (1 g each) of the powdered freeze-dried material were prepared in 20-mL (27 × 60 mm) glass vials on an analytical balance (Mettler AE 163). The samples were stored at 5, 10, and 20 °C in vacuum desiccators at relative humidity (RH) values ranging from 54 to 94%, achieved using saturated Mg(NO₃)₂, CoCl₂, NaCl, and KCl solutions (Greenspan, 1977; Labuza et al., 1985). The a_w values of the equilibrated samples at 23 °C were estimated with the GAB equation, using the average water content adsorbed at each storage condition. The extent of the nonenzymatic browning of triplicate 1-g samples was determined at intervals (Figure 4) up to 21 days, which was considered to be the maximum shelf life of most chilled foods. The samples were dissolved in water–ethanol (3:1) solution. The extent of browning was obtained as the optical density (OD) determined spectrophotometrically (Perkin-Elmer Lambda 2 UV–vis spectrometer) at 420 nm, which quantified the yellow and brown pigments formed at the final stages of the nonenzymatic browning reaction [e.g., Whistler and Daniel (1985)].

RESULTS

Water Adsorption. Both the BET and GAB isotherms could be used to model the experimental data (Figure 1). Experimental water adsorption values, as a function of water activity at 23 °C, for the food model are given in Figure 2. The BET and GAB monolayer values at 23 °C were both 3.6 g of H₂O/100 g of solids. Since the GAB model is generally accepted to model water adsorption of foods and is applicable over a wide a_w range (van den Berg and Bruin, 1981; van den Berg, 1986; Roos, 1993a), it was used to predict water contents at various browning conditions; e.g., the GAB model was used to calculate the a_w values at 23 °C for samples with known water contents at the lower temperatures. The water adsorption isotherm had a sigmoid shape typical of most food materials, with no indication of crystallization of the material due to water adsorption and plasticization.

Glass Transition Temperature. The glass transition temperature of the food model decreased with increasing water content. The decrease was similar to that for other biological materials (Slade and Levine, 1991) and for the maltodextrin component (Roos, 1993a), although the food model had lower T_g values at equal water contents, probably due to additional plasticization of the malto-dextrin by xylose and lysine. The measured T_g values of
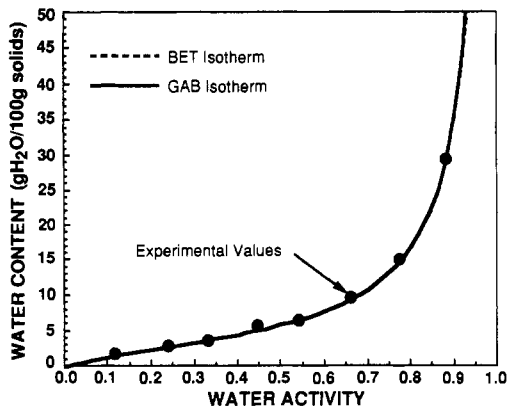
Figure 2. Sorption isotherm of the maltodextrin-based food model, with xylose and lysine (7% of solids, 1:1) as reactive compounds.
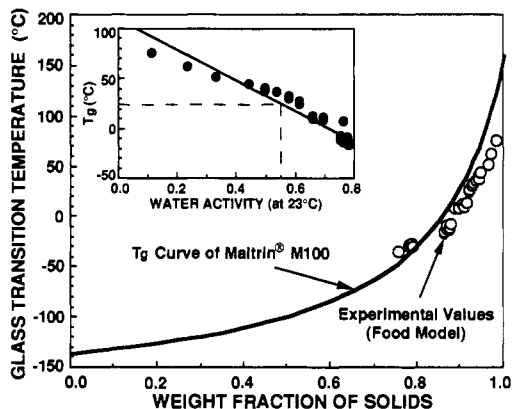

Figure 3. Glass transition temperatures (T_g) of the maltodextrin-based food model, with xylose and lysine (7% of solids, 1:1) as reactive compounds. The T_g values were lower than those of the maltodextrin alone [Maltrin M100; data of Roos and Karel (1991c)], probably because of plasticization of the matrix by xylose and lysine. The inset figure shows the linear decrease of T_g with increasing water activity.

the model, with the T_g curve of the maltodextrin, are shown in Figure 3. The T_g values also decreased linearly with increasing a_w (Figure 3), which has been found to be typical of materials plasticized by water (Roos, 1987; Slade and Levine, 1991; Roos, 1993a).

Nonenzymatic Browning. Nonenzymatic browning was observed to occur at all temperatures studied. The rate of pigment formation, as determined from the increase in optical density at 420 nm, was typical of that for food models with intermediate moisture contents [e.g., Warmbier et al. (1976)]. Plots of optical density against storage time showed a short initial induction period for most samples, which was followed by a linear increase in optical density, indicating zero-order kinetics (Figure 4). Slopes of the linear regression lines shown in Figure 4 were used as rate constants (k). The k value increased with increasing relative humidity at each storage temperature. The k value also increased with increasing temperature for samples stored above the same saturated salt solutions.

Nonenzymatic browning rates at various water contents and respective water activities at 23 °C are shown in Figure 5. The rate of browning increased with increasing water activity at each temperature studied. No rate maxima were observed in the a_w range studied, although the rate appeared to be leveling off at higher water activities in samples stored at 5 and 10 °C. This leveling off was more evident when the browning rate was plotted against water content of the samples (Figure 5). The browning rate as
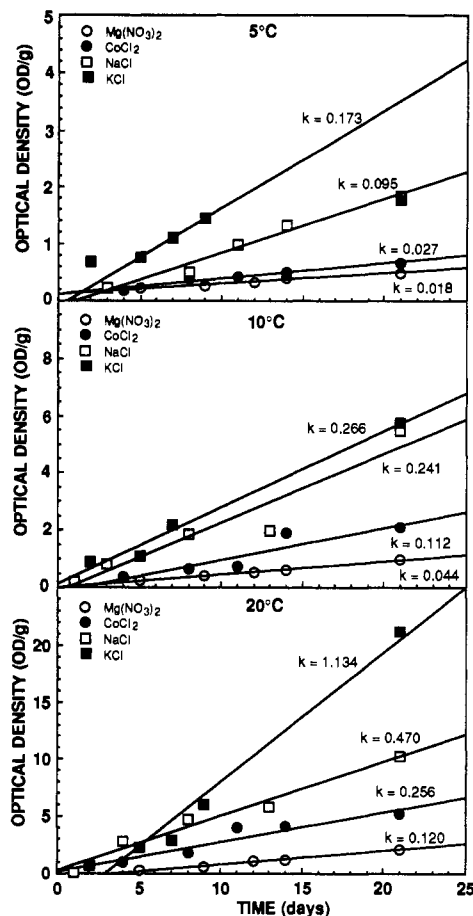

Figure 4. Optical density at 420 nm of the maltodextrin-based food model, with xylose and lysine (7% of solids, 1:1) as reactive compounds, at various storage times used in the determination of nonenzymatic browning rate. Linear regression analysis was used to obtain the rate constants (k), shown as the slopes of the regression lines. Saturated salt solutions were used to obtain various relative humidities at each temperature.
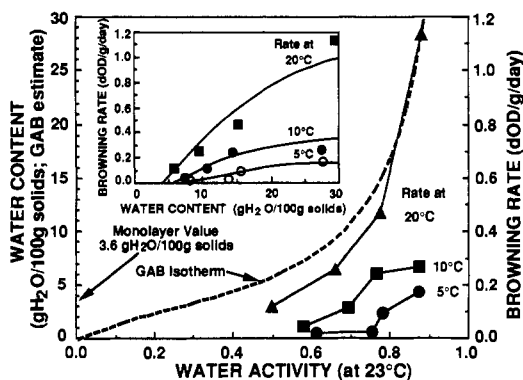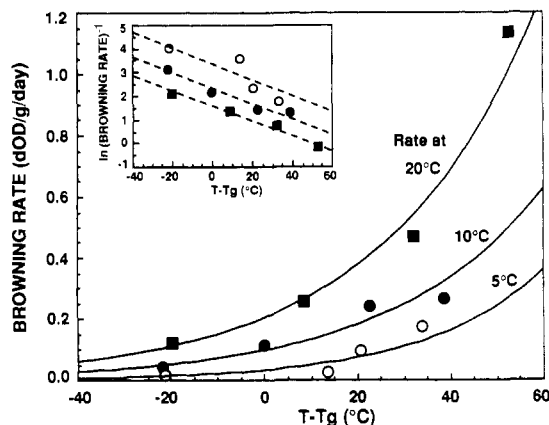

Figure 5. Nonenzymatic browning rate and water adsorption of the maltodextrin-based food model, with xylose and lysine (7% of solids, 1:1) as reactive compounds. The rate of browning increased with increasing water activity at each temperature and appeared to be leveling off at high water contents (inset).

a function of the temperature difference above the glass transition temperature ($T - T_g$) is shown in Figure 6. An exponential increase in the browning rate was observed with increasing $T - T_g$. Similar increases in browning rate with increasing $T - T_g$, for a wide range of dehydrated vegetables and food models, were reported by Karmas et al. (1992). Nonenzymatic browning was observed in samples stored below T_g, as also reported by Karmas et al. (1992). However, the rate of browning at temperatures above T_g was significantly higher than that below T_g, which

Figure 6. Temperature dependence of the nonenzymatic browning rate of the maltodextrin-based food model, with xylose and lysine (7% of solids, 1:1) as reactive compounds. At a constant experimental temperature, the rate of the reaction increased with increasing temperature difference above the glass transition temperature $(T - T_g)$. The Williams–Landel–Ferry (WLF) plot for temperature dependence of the reaction rate showed three separate lines (inset).

confirmed the drastic effect of $T - T_g$ on the browning rate constant noted by Karmas et al. (1992).

DISCUSSION

Results of the present study showed that the rate of nonenzymatic browning of the food model was affected by temperature and water content. An exponential increase in browning rate over the intermediate moisture range was observed at all temperatures (Figure 5). Although no rate maxima as a function of water activity (Labuza et al., 1970) were noticed, in accordance with the browning behavior of dehydrated cabbage (Mizrahi et al., 1970a), the increase in browning rate was highest at water contents or corresponding water activities that depressed the T_g to below the storage temperature (Figures 3 and 5). This finding agreed with that for browning rates in dehydrated vegetables and other food models in the vicinity of T_g (Karmas et al., 1992). It should also be noted that the rate of browning, over the temperature range studied, approached zero at moisture contents close to the BET monolayer value (Figure 5). The BET monolayer value has been considered to be a critical moisture level, above which the stability of dehydrated foods decreases [e.g., Labuza et al. (1970), Labuza (1980)]. However, nonenzymatic browning may occur at higher temperatures in anhydrous materials above T_g (Karmas et al., 1992), and the critical a_w and m values for stability, defined as those depressing T_g to below room temperature, are higher than the monolayer values (Roos, 1993a).

At a constant water content, the rate of nonenzymatic browning was found to increase significantly with increasing temperature, and at a constant temperature, the browning rate increased exponentially with increasing $T - T_g$ (Figure 6). Similarly, in a previous study (Karmas et al. 1992), browning data for vegetables and food models showed that the increase in browning rate as a function of $T - T_g$ was different at each water content and water activity. Those data suggested a strong dependence of the reaction rate on moisture and temperature. Karmas et al. (1992) connected the data points with solid lines at each water activity or water content, in a plot showing browning rate as a function of $T - T_g$. Such curves, when extrapolated to rates approaching zero, show a different $T - T_g$ value for each water content at which browning may occur. The moisture dependence of the reaction rate

at a constant $T - T_g$ was not discussed by Karmas et al. (1992). We believe that browning begins in the vicinity of T_g at each water content and shows an exponentially increasing rate with increasing $T - T_g$. This rate at a constant $T - T_g$, determined by moisture content and therefore by the extent of water plasticization, appears to increase with increasing temperature (Figure 6). In addition to temperature, moisture content, and physical-state effects on the browning rate, pH, reactants, and their concentrations may significantly affect the rate of non-enzymatic browning [e.g., Labuza and Baisier (1992)].

Food deterioration at low water contents may be related to physical changes; e.g., crystallization of amorphous compounds may affect the rate of browning (Saltmarch et al., 1981) or cause an increased rate of lipid oxidation (Shimada et al., 1991). In this study, crystallization of the amorphous matrix was unlikely, although other structural changes such as collapse, which would increase material density, may have affected browning rate, as was pointed out by Karmas et al. (1992). Such changes, however, are related to viscosity, which, in amorphous materials, decreases with increasing $T - T_g$, following the WLF-type temperature dependence (Slade and Levine, 1991; Roos and Karel, 1992). If the rate of nonenzymatic browning were similarly related to viscosity, the rate constant should increase with increasing $T - T_g$ according to eq 1, with

$$\ln \frac{k_{ref}}{k} = \frac{-C_1 (T - T_{ref})}{C_2 + (T - T_{ref})} \qquad (1)$$

$$k = k_0 e^{(-E_a/RT)} \qquad (2)$$

constants C_1 and C_2 solved as reported by Nelson and Labuza (1992). When T_g is used as the reference temperature (T_{ref}) with the corresponding reference rate constant $(k_{ref} = k_g)$, a plot of experimental values of $1/k$ against $T - T_g$ should give a single, continuous curve. Our data gave a separate line for each temperature (Figure 6). The lines had almost the same slope with a less dramatic effect of $T - T_g$ on the reaction rate than is typical of the WLF temperature dependence based on the "universal" values of C_1 and C_2 (Slade and Levine, 1991). Thus, eq 1 appears not to be in agreement with our experimental browning data.

The rate of nonenzymatic browning has often been modeled using the Arrhenius-type temperature dependence (eq 2) to successfully predict browning rates of various foods [e.g., Mizrahi et al. (1970b), Saguy et al. (1978), Stamp and Labuza (1983), Petriella et al. (1985), Franzen et al. (1990), Labuza and Baisier (1992)]. According to the Arrhenius equation, a linear relationship exists between ln k and $1/T$ (absolute temperature, k_0 is constant, R is gas constant). A plot of our experimental ln k values against $1/T$ showed four separate "lines" (Figure 7). Similar behavior has been reported for browning rates over a wide temperature range and at various water contents or water activities [e.g., Franzen et al. (1990), Karmas et al. (1992)]. The slopes of the lines obtained using linear regression analysis gave an average activation energy (E_a) of 83.6 kJ/mol (20 kcal/mol). This value is in good agreement with values, usually ranging from 80 to 130 kJ/mol (20–30 kcal/mol), reported in numerous studies for a wide range of foods and biological materials [e.g., Petriella et al. (1985), Labuza and Baisier (1992)]. It should also be noted that nonenzymatic browning probably occurs extremely slowly in freeze-concentrated amorphous food matrices. The temperature dependence of the reaction rate even for reactions with diffusional limitations
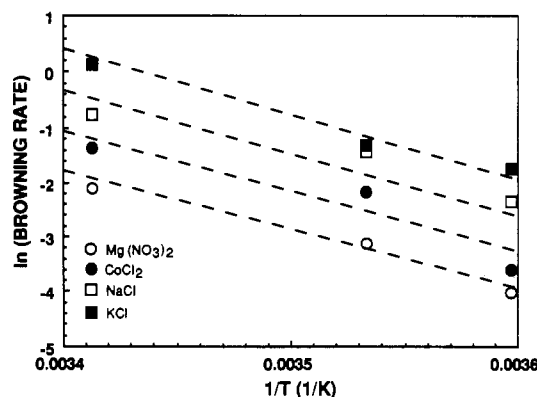
Figure 7. Arrhenius-type temperature dependence of the nonenzymatic browning rate of the maltodextrin-based food model, with xylose and lysine (7% of solids, 1:1) as reactive compounds. A separate line showing the moisture dependence of the reaction rate was obtained for samples stored at different relative humidities, achieved by using saturated salt solutions. The average activation energy (E_a) was 83.6 kJ/mol (20 kcal/mol).

(Karel et al., 1993) assures that the shelf life is not significantly reduced by the browning reaction. One example is ice cream, which contains browning reactants in a freeze-concentrated amorphous matrix and is usually stable well above the rate-controlling glass transition temperature.

Although the rate of nonenzymatic browning was considered not to follow the WLF equation, it appears that the reaction was inhibited at temperatures below T_g, probably because of diffusional limitations (Karel et al., 1993). The color formation observed below T_g was possibly due to nonhomogeneity of water plasticization of the matrix. Such behavior was also noted by Karmas et al. (1992), and it may be significantly affected by water produced during the reaction, collapse, or other structural changes. The rate-controlling effect of T_g was suggested by the fact that adjusting the T_g of the food model to below ambient temperature resulted in nonenzymatic browning at low temperatures. The rate of the nonenzymatic browning reaction could also be modeled, and it could be adjusted to proceed at a rate indicating the thermal history and the rate of quality loss of chilled foods.

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