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Kinetic model of the glucose–glycine reaction

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The kinetics of browning (measured in terms of the absorbance at 450 nm, A_{450}) in the glucose–glycine and 3-deoxyhexosulose (*DH*)–glycine reactions, and the kinetics of loss of sulphite species (*S(IV)*) in glucose–glycine–*S(IV)* reactions, all at pH 5.5 (acetate buffer) and 70°C, were used to derive, from first principles, a kinetic model for the browning of glucose–glycine mixtures. A consecutive 3-step reaction mechanism, in which glucose is converted to *DH*, which in turn is converted into an unspecified intermediate (*I*), the precursor of melanoidins, is described by the following three rate equations,

$$\frac{d[DH]}{dt} = k_1[\text{glucose}][\text{glycine}]$$

$$\frac{d[I]}{dt} = k_2[DH]([\text{glycine}] + 5.1[\text{glycine}]^2)$$

$$\frac{dA_{450}}{dt} = k_3[I]$$

where k_1, k_2 and k_3 are rate constants. The validation of this model is discussed critically. Experiments show that absorbance, in this system, varies with $(time)^3$ consistent with the integrated rate equations, but in contrast with the previously reported dependence on $(time)^2$. © 1997 Elsevier Science Ltd

INTRODUCTION

Undoubtedly, the Maillard reaction is one of the most complex reactions involving low-molecular-weight food components. It is known to give rise to hundreds of reaction products which are important as flavour volatiles, and a series of low and high molecular weight compounds, melanoidins, responsible for colour (browning). The latter have been only partially characterised. It is the object of many food processing operations to control colour and flavour development. On the whole, this is done through a knowledge of the empirical relationship between these attributes of food, the processing conditions and food composition. A relatively small number of investigators have attempted to address, directly, the idea that it should be possible to calculate the rate of browning, from first principles, using rate constants for individual reaction steps. The complexity of this task has been well described by Labuza (1994).

Arguably, the simplest Maillard reaction is that between glucose and glycine. It is established that the browning of glucose + glycine is a multi-step consecutive reaction; at pH 4–6 it involves the amine-assisted conversion of glucose to 3-deoxyhexosulose, *DH*, which reacts with glycine to form the pre-melanoidin subunits which polymerise to give the coloured melanoidins (Reynolds, 1963). The progress of browning is most commonly measured as the increase in absorbance at a single wavelength in the range, 420–490 nm. Whilst there is no unambiguous method to follow this reaction, the use of a single wavelength is perhaps more meaningful in the chemical sense than, for instance, the use of colour co-ordinate (Lab) values which give a measure of perceived browning. The main disadvantage in the use of single wavelength measurements is that the coloured products are a mixture of compounds with no absorption maximum in the range, 420–490 nm. Nevertheless, it has been common practice to attempt to relate such measurements to the rates and kinetics of the individual reaction steps involved in the sequence leading to melanoidins. With hindsight, we can now see that such an approach is unlikely to provide unambiguous mechanistic information.

Absorbance–time data for the glucose–glycine reaction show a characteristic 'induction' phase, when little

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browning occurs, followed by a rapid increase in absorbance. Polynomial expressions have generally been invoked to describe such absorbance–time relationships including the induction phase. One of the most relevant of these relationships is based on a consecutive 3-step mechanism (Haugaard *et al.*, 1951):

$$S + A \xrightarrow{k_A} I_1 \xrightarrow{k_B} I_2 \xrightarrow[A]{k_C} B$$

where S, A and B denote the reducing sugar, the amino acid and the product responsible for browning, respectively, I_1 and I_2 are intermediates and k_A, k_B and k_C are rate constants. The system of rate equations for this scheme was integrated for the situation where the reaction had reached a steady state with respect to I_1. It was assumed that the time required for the steady state to be established represented the induction time observed from the absorbance-time data. By way of hypotheses it was suggested that,

$$\frac{d[I_1]}{dt} = k_A[A][S]$$

$$\frac{d[I_2]}{dt} = k_B[I_1]$$

$$\frac{dB}{dt} = k_C[A][I_2]$$

and, in the steady state situation, $d[I_2]/dt$ is constant. Integration gives,

$$B = k'[A]^2[S]t^2$$

where k' is a combination of k_A, k_B and k_C. Experimental data for the browning of unbuffered (initial pH 6.1) glucose–glycine mixtures at 100°C behaved according to this equation up to an absorbance of 0.6 at 490 nm. Kato *et al.* (1969) used the relationship to demonstrate differences between the kinetics of the browning of glucose and fructose with glycine, and obtained a satisfactory linear plot of absorbance (at 470 nm) vs t^2 up to an absorbance of 4, with some deviation from this line at higher values (initial pH 5.5, unbuffered, 100°C). Measurement of the rates of loss of glucose and glycine (pH 7, phosphate buffer, 37°C) confirms the kinetics of the first step in their reaction to be of first order with respect to each substance (Baisier & Labuza, 1992).

In this paper we will aim to show that significant browning beyond the induction phase occurs well before any steady-state situation with respect to early intermediates is reached. To demonstrate this behaviour, it is necessary to consider the inhibition of the Maillard reaction by sulphite species, S(IV).

The browning of glucose is inhibited when S(IV) reacts with the intermediate 3,4-dideoxyhexosulose-3-ene, DDH, to form a relatively unreactive product 3,4-dideoxy-4-sulphohexosulose, DSH. DDH arises by the dehydration of DH. The kinetics of the glucose–glycine–S(IV) reaction have been investigated rigorously and shown to conform to a mechanism described by the following sequence of reactions:

$$\text{glucose} + \text{glycine} \xrightarrow{k_1} \text{DH} \xrightarrow{k_2} \text{I} \xrightarrow[\text{fast}]{\text{S(IV)}} \text{DSH}$$

where k_1 and k_2 are rate constants, and I is an unspecified intermediate. S(IV) inhibits the formation of Maillard products in general, and the inhibitor is regarded as reacting with the common precursor of these products. Since the reaction of S(IV) with DH is quantitative, we have developed the idea that a measure of the rate of conversion of S(IV) to DSH is also a measure of the rate at which glucose is converted into reactive intermediates in the uninhibited Maillard reaction. This idea underlies our new approach (Wedzicha *et al.*, 1994) to the study of the kinetics of browning and has successfully been applied to the browning of oligosaccharide mixtures (Wedzicha & Kedward, 1995). Essentially, S(IV) concentration-time data allow the values of k_1 and k_2 to be determined unambiguously and it has been shown that k_1 can exert a controlling influence over the rate of browning in the uninhibited reaction (Wedzicha & Kedward, 1995; Bellion & Wedzicha, 1993). The mechanism of browning involves additional steps beyond intermediate I, i.e.

$$\text{glucose} + \text{glycine} \xrightarrow{k_1} \text{DH} \xrightarrow{k_2} \text{I} \longrightarrow \longrightarrow \longrightarrow \text{B}$$

$$\text{fast} \Big| \text{S(IV)}$$

$$\downarrow$$

$$\text{DSH}$$

The overall kinetics of these later stages of browning could be investigated by measuring the rate of browning of DH.

This paper reports values of the rate constants k_1 and k_2, and considers the kinetics of the browning of DH. These results are used to obtain an integrated rate equation which is compared with absorbance-time data.

MATERIALS AND METHODS

Preparation of 3-deoxyhexosulose

The procedure used to prepare DH was that of Madson and Feather (1981). The purity of DH was measured by converting it to the corresponding metasaccharinic acid with limewater and then titrating the acid (Anet, 1961; Wedzicha & Kaban, 1986).

Preparation of reaction mixtures

Weighed amounts of the reactants and components of the buffer were dissolved in water. The initial pH was adjusted to 5.5 using acetic acid or 3 M NaOH, as appropriate. Solutions were made up to volume and

heated at 70°C. Two sets of glycine-containing reaction mixtures were used for the measurement of browning. The first set contained glucose (1.0 M) and glycine (0.2–1.0 M) in acetate buffer (0.5 M). The second set contained DH (4–20 mM) instead of the glucose. A third set of reaction mixtures contained glucose (1.0 M), glycine (0.5 M) and S(IV) (0.01–0.1 M) in the same buffer and was used to measure the rate of loss of S(IV).

Aliquots were taken at timed intervals and their absorbance at 450 nm was measured in 1 cm cells. Aliquots of reaction mixtures containing S(IV) were analysed for S(IV).

Measurement of total S(IV)

The loss of S(IV) was measured for reaction mixtures containing glucose, glycine and S(IV). The procedure was that of Humphrey *et al.* (1970) using 5,5′-dithiobis(2-nitrobenzoic acid) (Ellman's reagent DTNB) dissolved in phosphate buffer (pH 6.8). The absorbance of the S(IV)–DTNB mixture was measured at 412 nm. A standard curve was obtained using iodimetrically standardised solutions of S(IV).

RESULTS AND DISCUSSION

The Maillard reaction causes the release of H^+ and two contrasting reaction systems can be set up, with and without pH-control. The pH of unbuffered reactions, initially in the range pH 4–6, falls as the reaction proceeds. In this situation, there is not only a change, with time, in $[H^+]$, but also in the concentrations of the acid and conjugate base forms of the amino acid. These may have different tendencies to catalyse the Maillard reaction. At high temperature, the best method of pH-control is to use a buffer. It was decided to set up reactions in which the only variable was the concentration of the reactants and a buffered system was, therefore, chosen. It is recognised that the buffer species (acetic acid and acetate ion) are capable of acting as acid–base catalysts in the Maillard reaction (Saunders & Jervis, 1966) but their concentrations were kept constant throughout the investigation. In no experiment did the pH fall by more than 0.1 unit.

The spectrophotometric method for the analysis of S(IV) with DTNB (Humphrey *et al.*, 1970) at pH 7 measures the total S(IV) concentration, i.e. that which is free plus that which is bound reversibly to carbonyl groups, because hydroxysulphonates are decomposed at the pH of the reagent. The concentrations of glucose and glycine were chosen to be nominally 1.0 and 0.5 M, respectively, i.e. those concentrations used previously in model systems to obtain easily measurable rates.

Figure 1 illustrates the typical shape of a concentration-time graph for the loss of S(IV) from the reaction mixtures investigated in the present work. The slope of this graph, in the constant rate phase of the experiment,

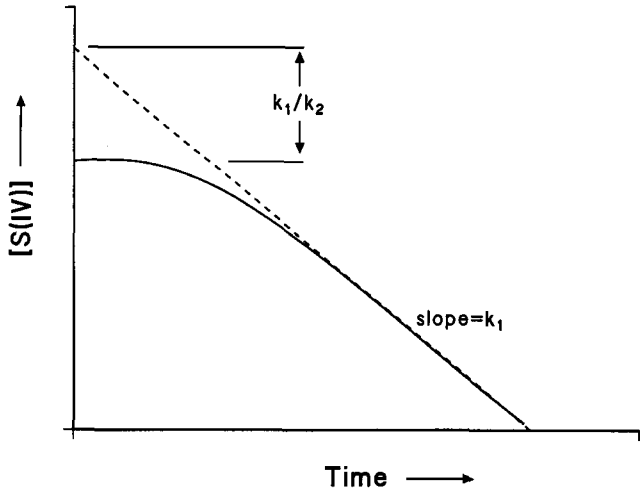

Fig. 1. Graphical method used to measure the values of k_1 and k_2 in the glucose–glycine–S(IV) reaction.

gives k_1 whilst k_2 can either be extracted from the data by fitting the integrated rate equation (Wedzicha, 1984) or from the geometry of the figure as illustrated here (Wedzicha & Garner, 1991).

The constant rate phase is reached when the concentration of DH reaches a steady state. Figure 2 compares the initial formation of colour in a glucose–glycine reaction as measured at the single wavelength of 450 nm with a [S(IV)]–time curve for a glucose–glycine–S(IV) reaction. It is striking that there is a significant (i.e. by 2 units) increase in absorbance whilst little of the S(IV) has undergone reaction (i.e. [S(IV)] has fallen by only 5% of its initial value). This implies that the end of the induction phase for browning does not signal steady state conditions with respect to the intermediates in question.

One experimental complication in the measurement of the values of k_1 and k_2, which apply in the absence of S(IV), is that the step described by k_1 is catalysed by

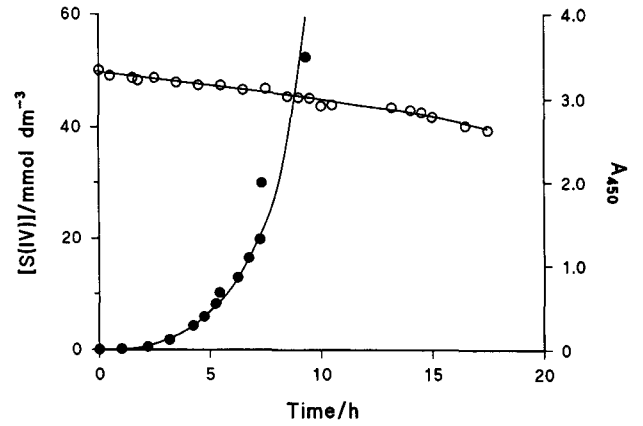

Fig. 2. Graphs of S(IV) concentration with time in the glucose–glycine–S(IV) reaction and absorbance at 450 nm (A_{450}) with time in the glucose–glycine reaction, to demonstrate the relative rates of these two changes. Reaction conditions: [glucose] = 1.0 M, [glycine] = 0.5 M, [S(IV)] = 0.05 M, pH 5.5 (0.5 M acetate buffer), 70°C. [S(IV)] ○; A_{450}●.

S(IV) (Wedzicha & Vakalis, 1988). In practice, this difficulty is resolved by measuring the apparent value of k_1 as a function of [S(IV)] and extrapolating the results to zero concentration. Using this approach, the rate law for the first step under the conditions adopted here is,

$$\frac{d[DH]}{dt} = 1.4 \times 10^{-3}[\text{glucose}][\text{glycine}] \text{ mol litre}^{-1} \text{ h}^{-1}$$

and for second step

$$-\frac{d[DH]}{dt} = \frac{d[I]}{dt} = 0.17[DH] \text{ mol litre}^{-1} \text{ h}^{-1}$$

Browning of 3-deoxyhexosulose

Preparation of DH was carried out by the specific method of Madson & Feather (1981); solutions of this intermediate were standardised by conversion to the corresponding metasaccharinic acid and titration with alkali (Anet, 1961). The product was also characterised as its 2,4-dinitrophenylhydrazone as described previously (Wedzicha & Kaban, 1986).

It has been shown (Wedzicha, 1984; Wedzicha & Garner, 1991) that, at 55°C, the concentration of DH in a glucose–glycine–S(IV) reaction is typically in the range 0-10 mM. In the present work on the kinetics of browning of DH, it was decided to vary the concentration of this intermediate in the range 4–20 mM to give a five-fold concentration change at a realistic level. Figure 3 shows the effect of DH concentration in the DH-glycine reaction on the increase, with time, in absorbance at 450 nm. The kinetics are seen to be quite different from the kinetics of the glucose–glycine reaction; the absorbance-time profile is typical of a simple (one rate-determining step) reaction and a maximum value of absorbance is reached, in contrast to a steadily increasing rate of browning in the Maillard reaction. This maximum value is accurately proportional to DH concentration and it is reasonable to assume that it represents the complete conversion of DH to melanoidins and other products, some of which may not be coloured. In principle, this experiment offers a new opportunity to obtain a *notional* extinction coefficient for the melanoidin, based on the number of DH molecules which have undergone reaction, assuming (in the calculation) that they are all incorporated into coloured products. In the present investigation it was found to be 1030 mol^{-1} l cm^{-1} which corresponds to $E^{1\%} = 58$ on the assumption that the melanoidins consist of five glucose-derived units (i.e., via DH) for every four glycine-derived units (Wedzicha & Kaputo, 1987).

Experimentally determined values of $E^{1\%}$ for non-dialysable ($M_r > 12\,000$) melanoidins have been in the range 30–50 (Wedzicha & Kaputo, 1992). The similarity of these results is striking and encouraging, and the higher value obtained here could reflect the fact that the mixture of products is expected to contain highly coloured substances of lower relative molecular mass than the non-dialysable component.

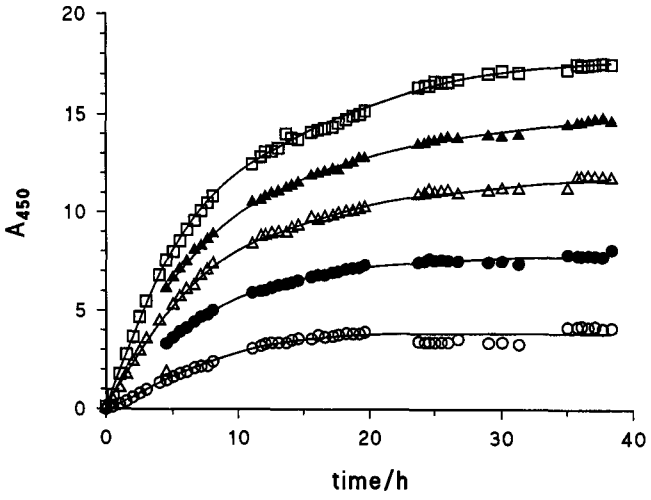

Fig. 3. Absorbance–time data for the DH-glycine reaction at different DH concentrations. Reaction conditions: [glycine] = 0.5 M, pH 5.5 (0.5 M acetate buffer), 70°C, [DH] = 3.22 mM ○; 6.45 mM ●; 9.67 mM △; 12.9 mM ▲; 16.1 mM □.

Figure 4 shows first order plots for the data plotted in Fig. 3 illustrating accurate first order behaviour over the major part of the reaction (> 90%), and confirmed by the fact that the first order rate constant (which is given by the slope) does not depend on DH concentration over a 5-fold range. The variation of this rate constant with glycine concentration is illustrated in Fig. 5. The intercept represents the rate of browning in the

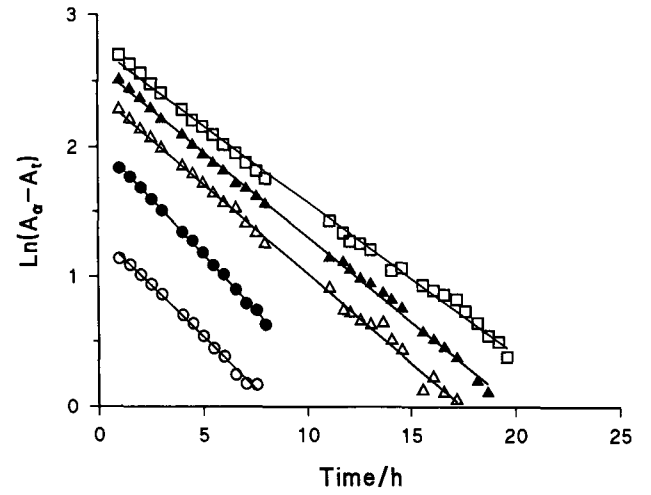

Fig. 4. First order plot for the browning of DH + glycine, at various concentrations of DH, shown as a graph of Ln $(A_\infty - A_t)$ *vs* time, where A_∞ is the absorbance at 450 nm after an infinite time and A_t is the absorbance at time t. Reaction conditions: [glycine] = 0.5 M, pH 5.5 (0.5 M acetate buffer), 70°C, [DH] = 3.22 mM ○; 6.45 mM ●; 9.67 mM △; 12.9 mM ▲; 16.1 mM □.

absence of glycine and, overall, it is seen that the rate of formation of colour in this step obeys the rate law:

$$\frac{dA_{450}}{dt} = 36[\text{DH}](1 + 5.1[\text{glycine}])\text{h}^{-1}.$$

Applying the 'molar' extinction coefficient of 1030 $\text{mol}^{-1}\,\text{l}\,\text{cm}^{-1}$ then, for a glycine concentration of 0.5 M, we obtain, $d[M]/dt = 0.12$ [DH] h^{-1}, where $[M]$ is a notional concentration of melanoidins, of course, making the important assumption that an unique value of extinction coefficient applies throughout the reaction. This rate equation corresponds well with that obtained for $d[I]/dt$ from kinetic measurements of the loss of S(IV) from glucose–glycine–S(IV) reactions (rate constant = 0.17 h^{-1}) under the same conditions. The slowest step in the conversion of DH to DSH occurs at a similar rate as the slowest step in the conversion of DH to melanoidins.

There are no kinetic data on the DH–glycine–S(IV) reaction at 70°C. Results obtained at 55°C (Wedzicha & Kaban, 1986) indicate that,

$$-\frac{d[DH]}{dt} = -\frac{d[S(IV)]}{dt}$$
$$= k(1+4.1[\text{glycine}])\ \text{mol dm}^{-3}\ \text{h}^{-1}$$

The relative magnitudes of the glycine-dependent and glycine-independent reactions, at 55 and 70°C, respectively, depend on their relative activation energies. However, the measured value at 55°C allows at least a comparison to be made of the magnitudes of the kinetic effects of glycine in the DH–glycine (5.1 mol^{-1} dm^{-3} from Fig. 5) and in the DH–glycine-S(IV) (4.1 mol^{-1} dm^{-3} in the equation above) reactions. The similarity is remarkable. This evidence, and the similarity of the rate constants in the two reactions, suggest that these values refer to the same chemical process, as implied by the concept of the kinetic model being investigated here.

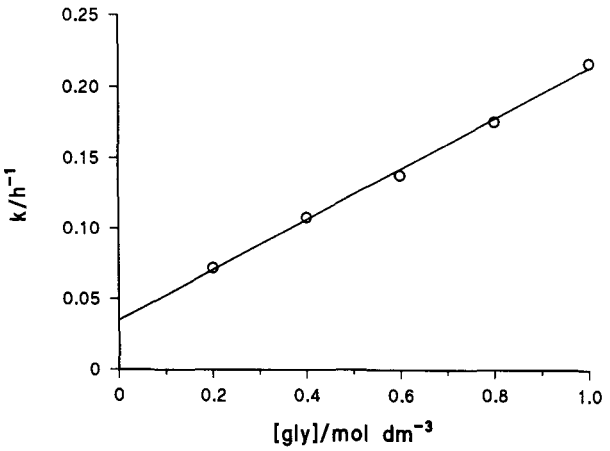

Fig. 5. Effect of glycine concentration on the first order rate constant, k, for the browning of DH at 450 nm. Reaction conditions: [DH] = 7.48 mM, pH 5.5 (0.5 M acetate buffer), 70°C.

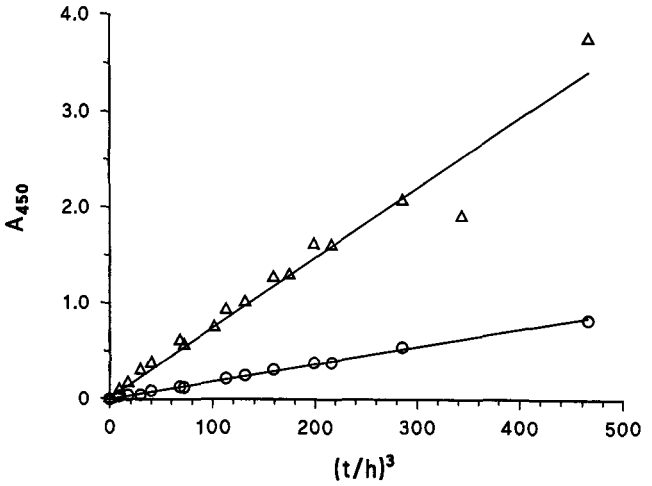

Fig. 6. Graph of absorbance at 450 nm vs $(\text{time})^3$ for the browning of glucose-glycine mixtures at different concentrations of glycine. Reaction conditions: [glucose] = 1.0 M, pH 5.5 (0.5 M acetate buffer), 70°C, [glycine] = 0.4 M ○; 0.8 M △.

Kinetics of browning of glucose–glycine mixtures

The results so far point to a 2-step consecutive mechanism defined by k_1 and k_2. By analogy with the integrated rate equation for the rate of loss of S(IV) in the glucose–glycine–S(IV) reaction (Wedzicha, 1984), we can write

$$B = k_1' t - \frac{k_1'}{k_2'}\left(1 - e^{-k_2' t}\right) \approx \frac{k_1' k_2'}{2} t^2$$

where the approximation is obtained by neglecting all terms beyond that in t^2 in the expansion of $\exp(1 - k_2' t)$, and k_1' and k_2' are k_1 and k_2 written as pseudo-zero order rate constants for clarity of presentation here. By

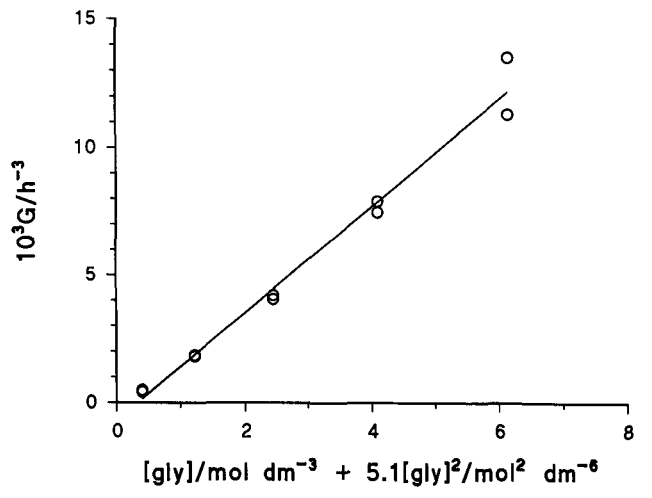

Fig. 7. Relationship of the gradient G of A_{450} vs $(time)^3$ graphs (as in Fig. 6), at various glycine concentrations in the range 0.2–1.0 M, to a function of glycine concentration derived from the kinetics of the DH–glycine reaction, using the data given in Fig. 5. Reaction conditions: [glucose] = 1.0M, pH 5.5 (0.5 M acetate buffer), 70°C.

putting in the known dependence of k'_1 and k'_2 on concentration, i.e:

$$k'_1 = k_1([\text{glucose}]\,\text{glycine}])$$

$$k'_2 = k_2[\text{DH}](1 + 5.1[\text{glycine}])$$

the theoretical rate equation for colour development is:

$$B \approx \frac{1}{2}k_1k_2[\text{glucose}]([\text{glycine}] + 5.1[\text{glycine}]^2)t^2$$

However, Fig. 6 shows that, for typical kinetic experiments at different glycine concentrations, the absorbance of glucose–glycine mixtures at 450 nm varies with (time)^3. The dependence of the gradient of these graphs on the concentration of glycine is illustrated in Fig. 7 for the full range of glycine concentrations. Similarly the order with respect to glucose concentration is 1. Thus, the observed kinetics follow closely the expression:

$$A_{450} = k[\text{glucose}]([\text{glycine}] + 5.1[\text{glycine}]^2)t^3$$

and the relationship between A_{450} and B is given by,

$$A_{450} = Bk_3t$$

where $k_3 = 2k/k_1k_2$. The slope of the line in Fig. 7 gives $k = 2.1 \times 10^{-3}$ when concentrations are measured in mol l^{-1} and time in h. Hence, $k_3 = 90$.

Significance of k_3

The kinetic model of browning in the glucose–glycine reaction involves two consecutive reaction steps which may be traced back to the rate-determining steps in the glucose–glycine–S(IV) reaction. This enables the individual rate constants to be measured with some degree of certainty. Unlike the browning of DH under similar conditions, browning in the glucose–glycine reaction appears to require an additional rate-determining step characterised by k_3 and which is of zero-order with respect to glycine concentration; its kinetic order with respect to the other components of the reaction has not yet been established. It is possible only to speculate on the type of reaction contributing to this reaction step and two examples are given to illustrate the possibilities.

First a linear increase, with time, in the overall extinction coefficient of the coloured products of reaction would give the expected behaviour. Second, integration of the equation for B with respect to time gives,

$$A_{450} = \frac{k'_1k'_2k_3}{6}t^3$$

providing that $\mathrm{d}(A_{450})/\mathrm{d}t = k_3B$, and the concentration of B at any instant can be regarded as that calculated simply from $\frac{1}{2}k'_1k'_2t^2$, i.e. the extent of conversion of the intermediate designated by B to the final product is small. The molecular mechanism of this process could involve the interaction of glucose, or an early Maillard intermediate which is present in the glucose–glycine reaction, but not in the DH–glycine reaction, with a precursor of the melanoidins formed from DH.

The formulation of the kinetics of both these additional steps gives rise to an overall three-step model of the same form as suggested originally by Haugaard *et al.* (1951). The reason why the integration of these 3 rate equations results in the extent of browning being proportional to (time)^2 and not (time)^3 is that these authors assumed that a steady state with respect to intermediate I_1 is reached. Removing this assumption leads to a dependence on (time)^3. However, the present approach is rigorous; it identifies a specific misconception with regard to steady state kinetics and the individual rate equations are based on measured kinetic behaviour of the individual reaction steps. The difference in the overall functional form of absorbance–time data reported here and that reported by Haugaard *et al.* (1951) or Kato *et al.* (1969), may be due to the fact that the present work involves buffered reactions. Other differences include a higher temperature (100°C compared with 70°C) in these earlier experiments.

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