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Relative Stability of Glucose and Fructose at Different Acid pH

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ABSTRACT

An empirical procedure is employed to assist in determining the relative stability of sugars at different pH. The procedure applies the most appropriate linear function for three arbitrary segments of the overall second order autocatalytic equation to sets of experimental data. As measured by the formation of 5-(hydroxymethyl)-2-furancarboxaldehyde (HMF) at 100°C, fructose is most stable between pH 4 and 6 and glucose between pH 2 and 6. However, fructose in its most stable environment is five times more reactive than glucose in its most stable environment.

INTRODUCTION

A continuing problem in ascertaining the relative stability of sugars in foods is lack of an acceptable procedure for making calculations in order to compare relative stability at different pH, temperature, time and sugar concentration. The problem has its origin in the fact that sugar decomposition reactions (dehydration, fragmentation, polymerization, etc.) are second order autocatalytic phenomena. Such reactions are characterized by rapidly increasing rate constants at the outset of the reaction, followed by rapidly decreasing rate constants at termination.

In practice, however, only partial segments of the overall second order autocatalytic kinetics are usually observed under a given set of reaction

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conditions. This communication describes an empirical procedure that permits comparison of partial components of second order autocatalytic rate kinetics regardless of whether the data conform to the induction, rapid or termination phase of the overall reaction. As an example the relative stability (or reactivity) of glucose and fructose at different pH, and as monitored by the formation of 5-(hydroxymethyl)-2-furancarboxaldehyde (hydroxymethyl furfural, HMF) is expressed numerically.

METHOD

Division of a second order autocatalytic reaction

A diagrammatic plot of a second order autocatalytic reaction (Frost & Pearson, 1961) with the rate expression $-dA/dt = kAB$ is shown in Fig. 1. The equation is obtained by integration of the afore-mentioned rate expression. In this study catalyst B is $[H^+]$ and A (the substrate) is either glucose or fructose. As one or more of the products (e.g. levulinic acid) is more acidic than the reactant, the rate increases as it builds up. The plot shown in the figure is empirically divided into three segments. Segment I prevails up until that time that the rapidly increasing rate of reaction ceases. Arithmetrically it corresponds to $y = kt^2$. Segment II encompasses a rapid but slowly diminishing rate and corresponds to $y = k\sqrt{t}$. For

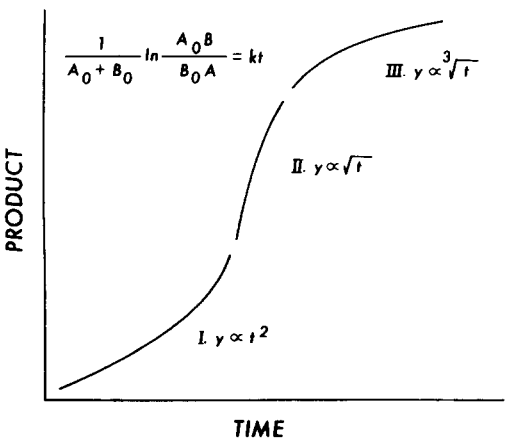

Fig. 1. Diagrammatic plot of a second order autocatalytic reaction divided into three segments wherein y is a linear function of t^n.

Segment III the rate is not nearly as rapid for II, and diminishes rapidly. It corresponds to $y = k\sqrt[3]{t}$.

Refluxing of sugars

Normal solutions of HCl were prepared to correspond to calculated pH 1–6 ($\pm 0{\cdot}1$ pH unit, actual). These were used to prepare 3% solutions of glucose and fructose. The solutions (500 ml) were then refluxed using a Glass-Cole heating mantel. Samples were taken at appropriate times, depending upon the initial pH employed. They were cooled and then frozen for subsequent HMF analysis.

Determination of HMF

HMF was determined by high pressure liquid chromatography (Model 7000, Micrometrics Instrument Co., Norcross, Georgia) equipped with a variable wavelength detector (Chromonitor 750) at 254 nm. The detector and strip chart recorder (Recordall 5000, Fischer Scientific Co., Pittsburgh, Pennsylvania) were connected in parallel to a dedicated computer (Type 3353, Hewlett Packard Corp., Avondale, Pennsylvania) suitable for acquisition of laboratory data. The sensitivity of the detector was set at 1·0 absorbance, while the recorder was set at 1 mV full scale and operated at 0·25 cm min^{-1}. A micro Bondapak C_{18} column, 300 mm × 3·9 mm ID, particle size 10 μm (Waters Associates Inc., Milford, Massachusetts) was maintained at 86 °C. The mobile solvent was high purity water, the flow rate 0·6 ml min^{-1} and the pressure maintained at 500 psi. The reservoir temperature was 65 °C.

The HMF (courtesy of Professor Milton Feather) employed had a molar extinction coefficient of 16 797. A standard solution containing 0·88 mg ml^{-1} was prepared and the program calibrated using a 10 microliter aliquot of the standard solution as an external standard. The retention time for the HMF under these conditions is 6·3 min and the precision $\pm 5\%$.

RESULTS

The formation of HMF from fructose at different pH at 100 °C is shown in Fig. 2. Differences between pH 4 and 6 ($< 4\%$) were not distinguishable;

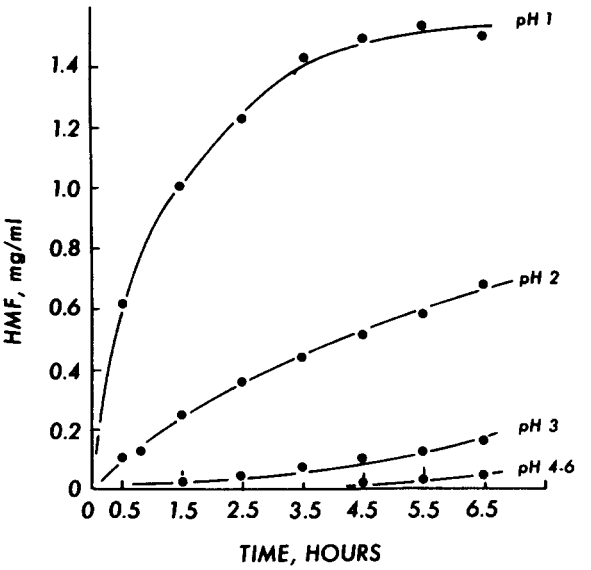

Fig. 2. Formation of HMF from fructose with time at 100 °C at various acid pH.

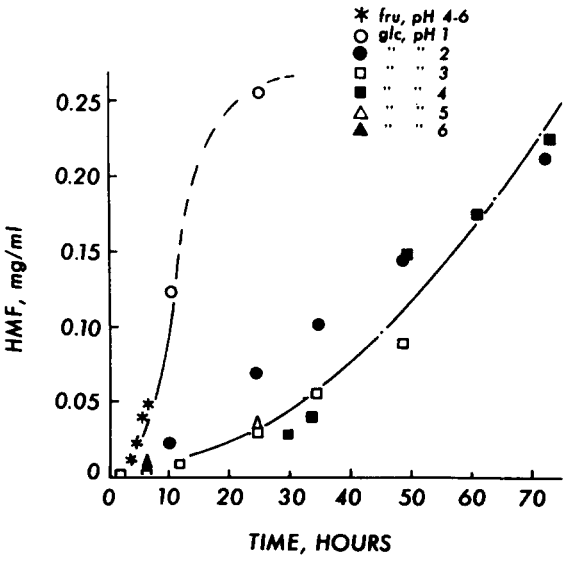

Fig. 3. Formation of HMF from glucose with time at 100 °C at various acid pH.

TABLE 1
Kinetic Characteristics for the Autocatalytic Transformation of Fructose to HMF at 100 °C at Different Hydrogen Ion Concentrations

pH (calculated)	*Division*	*Linear regression equation*	r^a	t/y	*Relative rate*
4–6	I	$y = 0{\cdot}001\,17t^2 + 0{\cdot}000\,3$	0·997	$\sqrt{0{\cdot}001\,17t}$	1·0
3	I	$y = 0{\cdot}003\,55t^2 + 0{\cdot}021\,8$	0·990	$\sqrt{0{\cdot}003\,55t}$	1·74
2	II	$y = 0{\cdot}312\sqrt{t} - 0{\cdot}137$	0·998	$(0{\cdot}312)^2$	9·17
1	III	$y^c = 1{\cdot}096\sqrt[3]{t} - 0{\cdot}25$	0·999	$(1{\cdot}096)^3$	38·8

[a] Coefficient of correlation.
[b] Unit t per unit y transformation in order to compare rate values using a common exponent.
[c] Up to 3·5 h.

therefore only the results obtained for pH 4 are shown. For a period of up to 6·5 h it can be seen that the data obtained for each initial pH level correspond to one of the three empirical segments for the overall second order catalytic reaction shown in Fig. 1. The linear regression equations for the divisions corresponding to each initial pH employed are given in Table 1. In all cases the regressions fit the empirical linear function with a correlation coefficient greater than 0·99.

In order to compare the relative rate of HMF formation from fructose at different pH, the root function for the slope of the linear regression was taken (column t/y in Table 1), and the rate found for fructose HMF formation at pH 4–6 used as unity. Thus, it can be stated that, at pH 3, the rate of HMF formation from fructose is about double that found at pH 4–6. At pH 2, it is about ten times as rapid, and at pH 1 it is nearly forty times as rapid.

Results obtained for glucose are shown in Fig. 3, where the time parameter was increased by a factor of ten in order to discern the course of the reaction (and with subsequent loss of apparent precision). For all practical purposes (and with the possible exception of pH 2), no significant differences in the rate of formation of HMF from glucose is apparent over the pH range 2–6. These data were therefore fitted to a single linear regression equation corresponding to empirical division I of Fig. 1. I is shown plotted in Fig. 2 and is $y = 4{\cdot}52 \times 10^{-5}t^2 + 0{\cdot}0069$. The coefficient of correlation is 0·970.

The results obtained for glucose at pH 1 were significantly different

TABLE 2
Propensity for the Formation of HMF from Fructose at Various pH Versus Glucose at Optimum Stability (pH 2–6)

pH	(*t*/*y fru*)/(*t*/*y glc*)	*Relative rate*
4–6	0·034 2/0·006 72	5·08 ×
3	0·059 5/0·006 72	8·85 ×
2	0·097 3/0·006 72	14·5 ×
1	1·330/0·006 72	198 ×

from those obtained at pH 2–6 however and, surprisingly, were of the same order as those obtained for fructose at pH 4–6, the range for which fructose is most stable. Thus, glucose in its most labile environment, reacts 0·0342/0·0064 (square root of 0·001 17 divided by the square root of $4{\cdot}52 \times 10^{-5}$) = 5 times as rapidly as in its most stable environment. By the same token, fructose, in its most stable environment, is five times as reactive as glucose in its most stable environment. In the most labile environment for each sugar (pH 1) fructose is about forty times as reactive as glucose. A direct comparison of fructose at various pH versus glucose at its most stable pH is shown in Table 2 as an example of the additional types of comparisons that may be made.

DISCUSSION

In order to execute a *kinetic* study of the acid stability of glucose versus fructose, it is clearly desirable to work at an acidity such that the hydrogen ion produced in the reaction is of minor importance and $[H^+]$ therefore remains essentially constant. In that case the reaction becomes simply first order. Rate constants obtained in this way are then proportionate to $[H^+]$ and if a study is done at a different pH, but with $[H^+]$ still in excess, a different first order rate constant will be obtained.

As applied to the stability of the sugars in foods, however, such kinetic studies are of questionable practical significance. In the first place, reactions of the type mentioned herein, which at times seem to obey the first order rate equation, are in fact pseudomolecular. Secondly, such reactions for sugars are qualitatively different at different pH, suggesting different reaction mechanisms of considerable interest. Finally, for food

chemistry studies, one cannot merely simply adjust to optimum conditions for first order reaction kinetics, but must be able to make comparisons wherein the kinetics are obviously different. This is the rationale behind the partitioning of the second order autocatalytic phenomenon shown in Fig. 1 into three parts.

Linear regressions might have been applied in a straightforward manner to the curvilinear data, for example in Fig. 2, but these regressions would obviously have been quite inaccurate. Therefore, it was decided to transform the data to the most appropriate linear function. It is not known at present whether the nearly ideal fits obtained are merely fortuitous, or have stoichiometric significance. In any event, the approach used seems to solve a problem which appears to be, in the final analysis, one reason for the paucity of data in the literature with respect to the relative stability of the sugars.

Heretofore, it was generally acknowledged that fructose was more reactive than glucose as the yield of HMF from sucrose was shown to be derived in its entirety from the fructose moiety of the disaccharide (Kiermayer, 1895). That glucose is not entirely inert in this respect became apparent when Alberda van Ekenstein & Blanksma (1910) were able to isolate, under standard conditions, 20–25% HMF from fructose and only 1% from glucose. Finally, Scallet & Gardner (1945) demonstrated that HMF is formed from glucose on refluxing in water alone.

The mechanism for the formation of HMF from glucose and fructose, whether the same or different, is very much in doubt, as is the intrinsic structure for the various tautomers for the two sugars in water solution. Data on the order of those presented here have application to these problems, and will serve as the basis for a future communication.

REFERENCES

Alberda van Ekenstein, W. & Blanksma, J. J. (1910). On ω-oxymethylfurfurol as the cause of some color reactions of hexoses, *Ber.*, **43**, 2355–61.

Frost, A. A. & Pearson, R. G. (1961). *Kinetics and Mechanisms*, John Wiley and Sons, New York.

Kiermayer, J. (1895). A derivative of furaldehyde from levulose, *Chem. Ztng.*, **19**, 1003–5.

Scallet, B. L. & Gardner, J. H. (1945). Formation of 5-hydroxymethylfurfural from D-glucose in aqueous solution. *J. Amer. Chem. Soc.*, **67**, 1934–5.