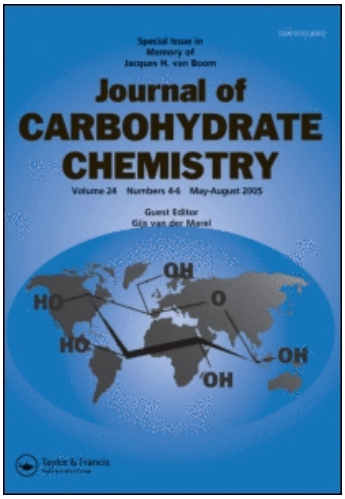

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Behavior of Water Structure-Breaking and Structure-Enhancing Solutes on the Thermal Degradation of Concentrated Solutions of Sucrose[1]

Gillian Eggleston[a]; John R. Vercellotti[a]; Les Edye[b]; Margaret A. Clarke[b]
[a] U.S. Department of Agriculture Research Service, Southern Regional Research Center, New Orleans, LA, USA [b] Sugar Processing Research Institute, Inc., New Orleans, LA, USA

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COMMUNICATION

BEHAVIOR OF WATER STRUCTURE-BREAKING AND STRUCTURE-ENHANCING SOLUTES ON THE THERMAL DEGRADATION OF CONCENTRATED SOLUTIONS OF SUCROSE[1]

Gillian Eggleston,[a*] John R. Vercellotti,[a] Les Edye,[b] Margaret A. Clarke[b]

[a]Southern Regional Research Center
U.S. Department of Agriculture Research Service
1100 Robert E. Lee Boulevard
P. O. Box 19687
New Orleans, LA 70179
USA

[b]Sugar Processing Research Institute, Inc.,
New Orleans, LA 70124
USA

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INTRODUCTION

Sugar losses result when sucrose in highly concentrated solution degrades under heat and other stresses in the factory and refinery and in manufacture of sugar containing products. Impurities such as salts, can increase the thermal degradation rate of sucrose under processing conditions, although literature sources conflict on the extent,[2,3,4,5] and the mechanism of action has still to be ascertained.

A number of reviews[6,7] have discussed the experimental data and current theories on the structure of water. Nearly all the theories consider water as a dynamic equilibrium mixture of non-bonded, discrete, highly reactive monomeric H_2O units and rigid, structured clusters of associated molecules $(H_2O)_n$ similar to those found in ice. Many solutes including carbohydrates appear very sensitive to this equilibrium, which can in turn be influenced by a third component, such as a simple

salt or solute.[8,9] The effects of solutes on water structure, summarised by Dobbins[10] and Fennema,[7] are largely determined by specific attractive forces between the solute and neighbouring water molecules, although detailed mechanisms are still a matter of debate. Large ions or solutes with considerable organic, hydrophobic character, *e.g.*, tetraalkylammonium ions and alcohols, respectively, which repulse water, act as water structure enhancers. The adjacent water molecules are oriented and hydrogen bonded by the water beyond them in bulk solution, with no counterattraction toward the solute ion. This results in a tightening of the water structure around the solute on the internal surface of the solvent cavity, *i.e.*, water structure is enhanced.

Hydrogen bonding solutes can have a separate, but equally marked, effect on water structure. When the distribution and orientation of a solute's hydrogen bonding sites are geometrically incompatible with those believed to exist in normal hydrogen bonded clusters in water, the solute frequently has a disruptive effect on normal water structure.[7] Guanidine-HCl and urea[7] are known examples, and tend to act as strong net water structure breakers. In comparison, sucrose fits well into the hydrogen bonded structure of water and is considered to act as a net water structure enhancer.[7] Furthermore, Clarke's[11] proposal that, in concentrated sucrose solutions, most of the water is associated in an hydration shell around the -OH groups of the sucrose molecule supports the concept of a highly ordered structure of solution. The first step in acid degradation of sucrose is protonation of the glycosidic oxygen[5] to form a sucrose oxonium ion, which is the precursor to subsequent degradation product formation. The degree of water structure around the hydrated sucrose molecule would be expected to affect the mobility and activity of protonated water and, therefore, affect the initial first protonation step of degradation.

Here, we report an initial study to elucidate the role of water structure in salt catalysis of the initial thermal degradation of concentrated solutions (~65°Brix or % weight dissolved solids) of sucrose which are common in sugar manufacture, using the water-structure enhancers[10] ethyl alcohol, *tert*-butyl alcohol and tetramethylammonium chloride, and water structure breakers urea[7] and guanidine HCl. Model reactions were undertaken without buffers to reduce interfering ion affects and assess the contribution of natural pH changes.

RESULTS AND DISCUSSION

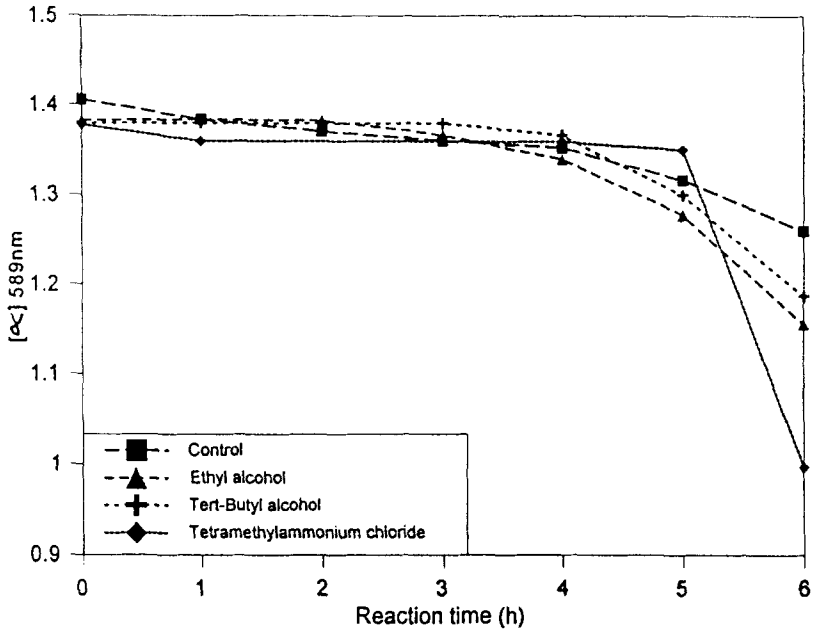
Very little sucrose degradation was observed in the model system containing only sucrose (control), over the first 4 h (approx. 3.8%), with subsequent accelerated degradation from 4-6 h (see Fig. 1). The initial lag phase is slow but finite. The first step in acid degradation of sucrose is protonation of the glycosidic oxygen[5] to form a sucrose oxonium ion which undergoes a scission reaction to produce a glucose and a fructose carbocation intermediate. The carbocation is lost by several reaction channels:[5] it may add a hydroxyl ion from water to produce fructose; or add to one of the hydroxyl oxygens of another saccharide (mostly sucrose) molecule to form oligosaccharides;[12]

undergo non-specific degradation to a range of secondary products including organic acids and 5-hydroxymethylfurfural; cyclize to form the anhydride. The initial trace amounts of organic acid secondary products formed, such as formic and levulinic acids, induce the accelerated degradation curve (Fig. 1) by further protonation of sucrose,[5] and the ensuing organic acid formation is responsible for inducing the pH drop during accelerated degradation reaction time (in this example pH dropped from 6.46 to 5.13 across 6 h total reaction time).

The effects of the water structure enhancers ethyl alcohol and tetramethylammonium chloride on initial sucrose degradation, as monitored by optical rotation (OR), are shown in Fig. 1. The pH of the ethyl alcohol-sucrose solution decreased from 6.44 to 4.54; therefore, although initial acid production occurred in the form of protonated hydronium ions, sucrose degradation was still relatively depressed; this indicated that increased water structure around the sucrose had a stabilizing effect on initial thermal degradation by repressing hydronium ion activity. As expected, the larger and more hydrophobic *tert*-butyl alcohol had a slightly greater stabilizing effect than ethyl alcohol, because the water adjacent to the non-polar hydrophobic *tert*-butyl groups becomes more structured in an amount approximately proportional to the size of the non-polar region.[8,10] These effects were more striking when pseudo-first order kinetics of initial degradation over the lag phase period, as measured by OR and ion chromatography with integrated pulsed amperometric detection (IC-IPAD), were calculated (see Table I). Sucrose hydrolysis has been shown to be a function of the concentration of sucrose and water.[3,13,14] As water is present in excess, the fraction of water used in the reaction is negligible and a pseudo-first order reaction rate law with respect to sucrose concentration is followed.[14] Within experimental error, ethanol did not significantly increase initial degradation as measured by OR and IC-IPAD.

IC-IPAD is an accurate technique to measure sucrose degradation kinetics because it measures actual sucrose, glucose and fructose, but can be tedious to operate. In comparison, the measurement of sucrose by OR is more convenient and is still used by the majority of the sugar industry. It is very precise provided that no other optically active compounds are present; and this assumption was made, especially where no color changes were apparent. However, as seen in Table I, the hydrolytic rate values of initial sucrose degradation as measured by OR were, in general, significantly lower that those calculated from IC-IPAD data. Similarly, Manley-Harris et al.[15] observed a small but significantly lower rate value for the alkaline degradation of a dilute 4% sucrose solution using OR compared to gas chromatography. These findings suggest that trace compounds with a high positive rotation may have been present. The OR data may, therefore, have introduced an absolute error in the rate measurements, but the pattern was generally the same for OR as IC-IPAD.

In the tetramethylammonium chloride-sucrose solution, there was a slight but steady increase in pH from 6.04 to 8.26 over the first 5 h while sucrose degradation was depressed, as monitored by OR (Fig.1). However, a closer inspection of the initial kinetic rate, as monitored by IC-IPAD



a. OR: change in optical rotation at 589nm as described under **Polarimetry** in the **EXPERIMENTAL** section.

Fig. 1. Effect of water structure enhancers on the degradation of sucrose, as monitored by OR[a]

TABLE I. Effect of water structure enhancers and breakers on degradation of concentrated sucrose solutions: pseudo-first order kinetic data.

	Initial Kinetic Constants at 100 °C[a]			
Sample	Polarimetry		IC-IPAD	
	K_1 ($sec^{-1} \times 10^{-6}$)	Std. error $\times 10^{-6}$	K_1 ($sec^{-1} \times 10^{-6}$)	Std. error $\times 10^{-6}$
Control (no salt)	2.61	0.30	3.82	1.04
Ethyl alcohol	1.11	0.36	4.2	0.08
Tert-Butyl alcohol	0.54	0.23	nd[b]	---
Tetramethylammonium chloride	2.10	0.42	18.55	3.27
Urea	13.04	---	50.00	---
Guanidine-HCl	22.00	0.59	25.59	1.34

a. The time range over which the initial kinetic constant range was measured varied from sample to sample.
b. nd = not determined

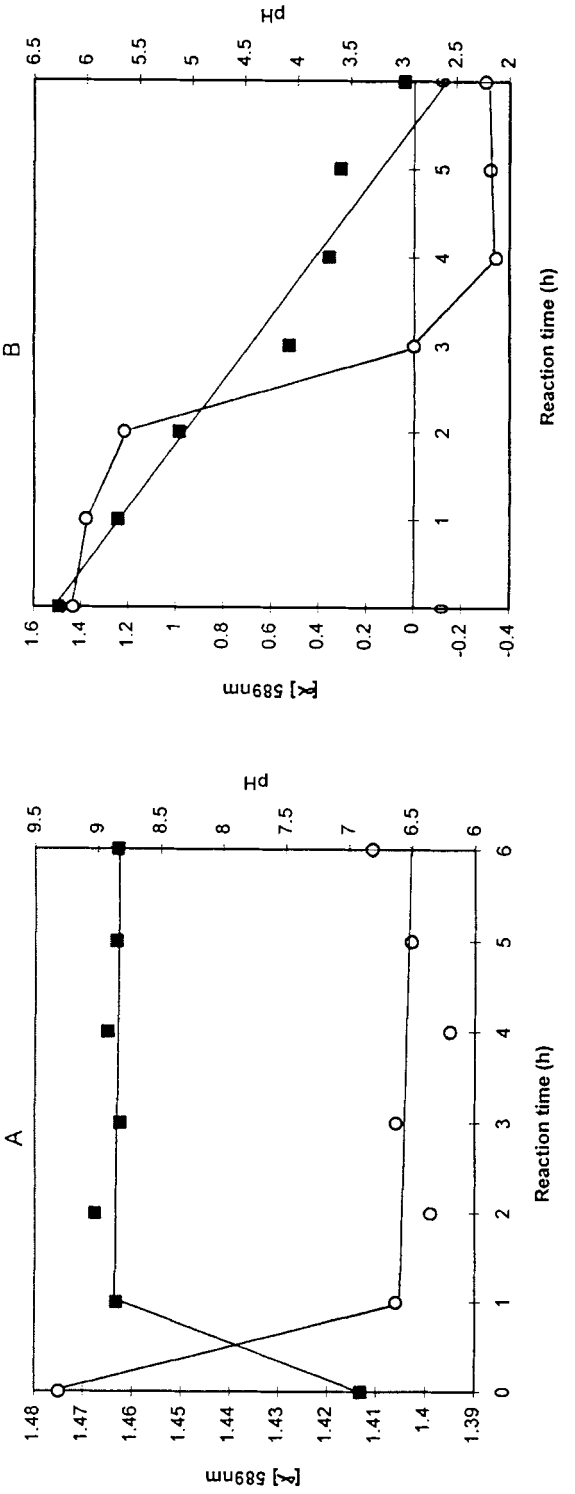
indicates that significant degradation did occur. From 5 to 6 h there was a marked drop in pH from 8.26 to 4.38, indicating accelerated degradation had been induced, which explains the concomitant decrease in OR (Fig.1). Although tetramethylammonium chloride has hydrophobic character like ethanol, it is also more ionic. As the mechanism proposed[5] for sucrose degradation is heterolytic it may be possible that the higher dielectric constant contributed to higher hydronium ion activity and increased degradation and was more critical than water structure effects.

Effects of the hydrogen bond/water structure breakers guanidine-HCl and urea, are illustrated in Fig. 2. The kinetic data are listed in Table I. Guanidine-HCl markedly increased sucrose degradation over 6 h with a concomitant rapid decrease in pH (see Fig. 2) and after 4 h a pale yellow color was produced, clearly indicating that acid degradation had occurred. In marked comparison, urea only increased sucrose degradation over the first hour when the pH was favorable for acid degradation.[3] Urea thermal hydrolysis produces ammonia; consequently, an alkaline solution (~pH 8.9) formed, which caused significant alkaline stabilization of the sucrose (see Fig. 2), as measured by OR and IC-IPAD. Sucrose is known to be relatively stable under alkaline conditions[2] because it lacks the unsubstituted hemiacetal grouping present in reducing disaccharides. The pale yellow colored solution observed after only 2 h was undoubtedly because of Maillard type browning reactions between traces of reducing sugars and ammonia. Therefore, under acid degradation pH conditions, *i.e.*, less than pH 8.3,[3] urea increased sucrose degradation; since urea is non-ionic, it would not be expected to affect the thermal stability of sucrose by electrostatic principles. Therefore, reduced water structure must have played a role in increased sucrose degradation; however, under alkaline conditions, pH effects were more critical.

In conclusion, these model experiments suggest that a manipulation of the water structure around a sucrose molecule in concentrated solution can affect thermal degradation, especially under non-ionic and acid degradation conditions. However, pH effects are more critical than water structure changes. Further work with salts will be published as a full paper. Currently, additional studies are in progress to confirm salt versus pH effects, where pH is kept constant over reaction time by using an automatic titrator.

EXPERIMENTAL

Sucrose Degradation Model Systems. Model systems consisted of molar sucrose-water-salt/solute ratios of 1:10:0.05M respectively (equivalent to a sucrose concentration of ~65°Brix). Salt concentrations of 0.05M were used, because preliminary experiments had indicated significant and measurable degradations occurred at this concentration, and for comparison with Richard's[5] results. Waters of hydration of certain salts were taken into account when calculating the amount of water (resistance of 18 megaohms) added. Sucrose was first dissolved in water at room temperature (~25 °C), and then salt added. Portions of the reaction solutions (3 mL) were distributed



a. OR: change in optical rotation at 589nm as described under Polarimetry in the EXPERIMENTAL SECTION.

Fig.2. Effect of (A) urea and (B) guanidine-HCl on the degradation of sucrose. -o- OR[a] and -■- pH

in 5 mL Pierce Reactivials™, and sealed with Teflon septa. To avoid oxidative degradation of substrates, Reactivials were flushed with pure, dry nitrogen. Reactivials were then placed in an oven at 100 °C for the required time. After removal from the oven the samples were allowed to cool, and then diluted by weight for polarimetry and ion chromatography analyses.

Materials. Sucrose, guanidine HCl, urea and tetramethylammonium chloride were Baker analytical grade. Absolute dehydrated ethyl alcohol and absolute *tert*-butyl alcohol were high purity grades from Quantum Chemical Corp. and Fisher Scientific Co., respectively.

pH Measurement. pH of the non-diluted samples was measured at room temperature (~25 °C) on a calibrated Markson model 4603 Solution Analyzer after 10 mins.

Polarimetry. Samples were diluted by a weight of water and their optical rotation (pol) measurements recorded at 589 nm, in a 10 cm pathlength cell, on an Optical Activity Limited AA10 Polarimeter, calibrated in International Sugar Scale (ISS) at room temperature (~25 °C). Results are expressed as specific rotations $[\alpha] = \alpha / C \times L$, where α=measured rotation, C=concentration of sugar (g/100 mL of solution), L=cell length(dm).

Ion Chromatography. Carbohydrate (sucrose and degradation products) concentrations were determined by ion chromatography (IC) using a Dionex (Sunnyvale, CA, USA) BioLC instrument. Carbohydrates were separated on Dionex CarboPac PA guard (25 x 4 mm) and PA-1 analytical (250 x 4 mm) anion exchange columns, at a flow rate of 1.0 mL/min at ambient temperature (~25 °C). Column eluant conditions were: 16 mM NaOH isocratic (inject; 0.0-2.0 min), a gradient of 16-160 mM NaOH (2.0-35.0 min), followed by isocratic 200 mM NaOH (35.1-37.0 min), and return to 16 mM NaOH (37.1-50.0 min) to re-equilibriate the column with the initial mobile phase prior to the next sample injection. Detection used was integrated pulsed amperometric detection (IPAD). The detector was equipped with Au working and Ag/AgCl reference electrodes, operating with the following working electrode pulse potentials and durations: E_1=+0.05V (t_0=0.00 sec), E_2=0.05V (t_1=0.42 sec), E_3=+0.75V (t_3=0.43 sec), E_4=+0.75V (t_4=0.60 sec), E_5=-0.15V (t_5=0.61 sec), E_6=-0.15V (t_6=0.96 sec). The duration of the IPAD integration interval was set at 0.2-0.4 sec. Using a Spectra-Physics SP8880 autoinjector and Dionex AI-450 chromatography software, runs were accumulated from multiple model kinetic samples and standards. The standards were glucosamine-HCl (internal standard), glucose, fructose, sucrose, raffinose and stachyose. Ten different levels of the standards were staggered across the sample runs, and standard curves were generated from 0.5 to 380 ppm to test linearity in multiple runs and generate area response factors. Samples were run in duplicate. Response factors were generated for each of the carbohydrates in the model kinetic sample mixture.

Kinetic Analyses. Kinetic raw data obtained from polarimetry and IC-IPAD were used to calculate first order rate constants by use of a linear, least squares computing method.

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