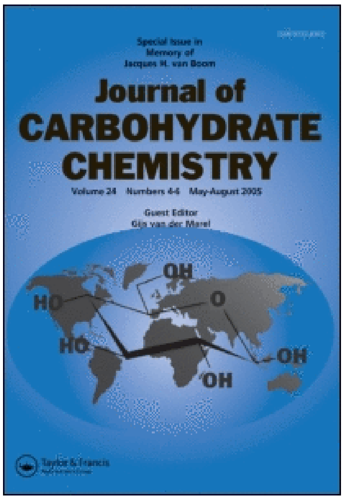

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EFFECTS OF SALTS ON THE INITIAL THERMAL DEGRADATION OF CONCENTRATED AQUEOUS SOLUTIONS OF SUCROSE[1]

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ABSTRACT

The effects of salts and other solutes on the degradation of highly pure sucrose in concentrated aqueous solutions (~65 °Brix or % dissolved solids) at 100 °C were investigated. Polarimetry and ion chromatography with pulsed amperometric detection (IC-IPAD) were used to quantify sucrose degradation. Pseudo-first order kinetic constants of initial degradation rates were calculated. Salt and solute effects were first considered with relation to their effect on water structure around the sucrose molecule. Na^+, Mg^{2+} and Ca^{2+}, which act to enhance water structure, slightly increased initial degradation; the latter two ions significantly increased subsequent accelerated degradation. Highly charged, small cations, e.g., Al^{3+}, significantly increased sucrose degradation through polarized hydrated ions/acidic pH effects. Larger cations, e.g., K^+, which act to reduce water structure, significantly increased degradation. The Hofmeister (lyotropic) anion order was not followed for sucrose thermal degradation effects, which indicated that anion binding to hydrophobic sites on the sucrose molecule is not critical. Other possible mechanisms of salt-induced sucrose thermal degradation are discussed.

INTRODUCTION

Chemical losses of sugar result when sucrose in highly concentrated solution degrades under heat and other stresses in the factory and refinery and in the manufacture of sugar containing products. Impurities such as salts are known to increase the thermal degradation rate of sucrose under processing conditions, although literature sources conflict on the extent of this,[2,3,4,5] and the mechanism of action has still to be ascertained. Consequently, kinetic data are needed to predict better the kinetics of sucrose losses, in the presence of salts under conditions of manufacturing concentrations and temperature. Parker[3] observed that increasing ionic strength up to 2M as KCl or 1M as $MgCl_2$ increased the rate of sucrose degradation over a wide range of sucrose concentrations (6.8-69.0 °Brix or % dissolved solids), temperatures (25-80 °C) and pH's (1-6); he claimed the salt effect was not significant. In contrast, Clarke[4] in early studies on the use of HPLC (High Performance Liquid Chromatography) to measure sucrose degradation rates, observed that when reactions were run at 0.1M KCl in concentrated sucrose solutions (60 °Brix) at pH 7 and 90 °C, there was a 3.5 fold increase in the rate of degradation compared to reaction without the added salt. Richards,[5] working with ~70 °Brix sucrose solutions at 100 °C and 0.05M salt, also observed marked increases in degradation rates in the presence of certain salts. $MgCl_2$ dramatically accelerated sucrose degradation, as did $CaCl_2$ and NaCl but to lesser extents. Richards[5] proposed that the increase in degradation rate was caused by enhanced withdrawal of electrons from the glycosidic oxygen of the sucrose molecule by protonation of the acetal oxygen with the hydrated magnesium ion.

A useful approach for an advanced understanding of the mechanism of thermal degradation of sucrose in the presence of salts and solutes would be to clarify the role of water structure in the thermal degradation of sucrose. A number of reviews[6,7,8] have discussed the experimental data and current theories on the structure of water. Nearly all theories consider water as a dynamic equilibrium mixture of non-bonded, discrete, highly reactive monomeric H_20 units and rigid, structured clusters of associated molecules $(H_20)_n$ 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.[9,10] To explain the reactivity or lack of reactivity of a solute on a carbohydrate system it is, therefore, necessary to consider the effect of the species upon bulk water properties.[11] The effects of simple electrolytes and other solutes on water structure, summarised by Dobbins[11] and Fennema,[7] are largely determined by specific attractive forces between the solute and neighboring water molecules, although detailed mechanisms of these effects are still a matter of debate.[6,7,8] Three distinct classes have been postulated: (1) Small or highly charged ions, e.g., Al^{3+}, Mg^{2+}, Ca^{2+}, Na^{+} and Li^{+}, which attract water through strong ion-dipole forces. The ions act as nuclei for cluster formation by immobilizing the surrounding water molecules, and this attractive force extends beyond the nearest neighbors, resulting in high local water structure centered around the solute ion. (2) Larger, monovalent ions, e.g., K^{+} and Rb^{+}, which have weaker electronic fields, and therefore relatively weaker attractive forces to the surrounding water, which leads to fewer immobilized water molecules in the areas of these ions. The overall effect is a reduction of structured water clusters, although the effect is minimal[7] with K^{+}. (3) Large ions or solutes with considerable organic, hydrophobic character, e.g., tetraalkylammonium ions and alcohols, respectively, which repulse water. 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, in a 65 °Brix sucrose solution (common in sugar factories and refineries), the sucrose is approximately 3M and the water 30M, i.e., there is a ratio of one sugar molecule to ten water molecules.[12] Since water exists in tetrahedral groups, there are approximately two of these groups to each sugar molecule. Therefore, most of the water is associated in a hydration shell around the -OH groups of the sucrose molecule, and the ratios support 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. We recently described the affects of ethyl alcohol and tetramethylammonium chloride, water structure enhancers, and guanidine-HCl and urea, water structure breakers, on the degradation of concentrated solutions of sucrose (~65 °Brix) at 100 °C.[13] Only ethyl alcohol, which has hydrophobic and non-ionic character, markedly stabilized sucrose.

Conversely, guanidine-HCl and urea significantly increased degradation, although in alkaline conditions pH effects were more critical than water structure effects.[13]

Since the pioneering work of Hofmeister almost a century ago, it has been recognised that some salts, generally in a well defined order (the lyotropic series[14]), can stabilize certain macromolecular conformations in aqueous solution, drastically alter the kinetics of organic chemical reactions in solution, and cause other phenomena in the fields of physical chemistry.[11,14] How these salts influence the stability of macromolecules in water is considered to be related to the ability of a particular ion to bind to a relatively hydrophobic site.[11,15] A change in the hydrophobic segment-solvent repulsive forces affects the delicate balance of intermolecular interactions that determine macromolecular stability in solution. A study of the Hofmeister series of anions may, therefore, offer some additional insight into the mechanism of sucrose degradation.

This study uses model sucrose-salt/solute systems to determine the kinetic constants of initial degradation rates of concentrated solutions of sucrose (~65 °Brix) at 100 °C, under nitrogen. Salts and solutes studied included salts commonly found in sugar processing factories and refineries, and those which would aid further elucidation of the chemistry of salt effects. Degradation of sucrose was quantified by polarimetry (optical rotation or OR) and ion chromatography with integrated pulsed amperometric detection (IC-IPAD) methods. Model reactions were undertaken without buffers to eliminate interfering ion effects and to assess the contribution of natural pH changes.

RESULTS AND DISCUSSION

In order to study model sucrose-salt/solute thermal degradation systems, it was necessary to obtain a highly pure sucrose source, with low indigenous concentrations of cations that are common in commercial sugar refineries and factories[16] and are known to affect degradation.[2,4,5] Sucroses from industrial, biotechnological and analytical grade sources were first studied for potassium, calcium, magnesium, zinc and iron cation contents, using atomic absorption spectroscopy. Baker™ analytical sucrose (from sugar cane) was the most acceptable (in mg/kg: calcium 2.1; magnesium 0.9; potassium 5.4; zinc 3.2 and iron 0.7).

Very little sucrose degradation was observed in the model system containing only sucrose (control) in a ratio of 1 mol sucrose:10 mol water over the first 4 h (~3.8%), with subsequent accelerated degradation from 4-6 h (Fig. 1). The initial lag phase is slow but

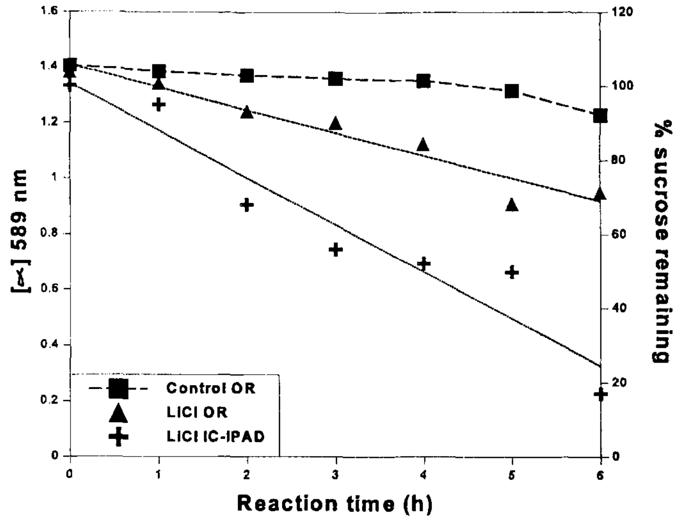

Fig.1. Effect of lithium chloride on sucrose degradation at 100°C, as monitored by OR[a] and IC-IPAD

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

finite. The first step in acid degradation of sucrose is protonation of the glycosidic oxygen[5] to form a sucrose oxonium ion that undergoes a scission reaction to produce a fructose carbocation and glucose. 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,[17] undergo non-specific degradation to a range of secondary products including organic acids and 5-hydroxymethylfurfural, and 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).

Salt/solute catalysis experiments were first considered in relation to their effect on water structure around the sucrose. All model sucrose-salt systems consisted of 1 mol sucrose:10 mol water: 0.05 mol salt. Salt concentrations of 0.05M were used (as in Richards[5]) because preliminary experiments had indicated significant and measurable degradations occurred at these concentrations. The first class of salts studied was small or highly charged cations that attract water and enhance overall water structure, e.g., Li^+,

Table. Effect of monovalent, divalent and trivalent chlorides on degradation of concentrated sucrose solutions.

Initial pseudo-first order kinetic constants at 100 °C[a]				
	Polarimetry		IC-IPA	
Salt added (0.05M)	**k_1 (s^{-1} x 10^{-6})**	**Std. error x 10^{-6}**	**k_1 (s^{-1} x 10^{-6})**	**Std. error x 10^{-6}**
Control (no salt)	2.6	0.3	3.8	1.0
LiCl	20.0	0.3	69.0	26.0
NaCl	3.0	---	12.2	---
KCl	5.4	1.8	18.0	---
RbCl	4.8	---	17.5	---
$MgCl_2$	1.5	0.3	11.0	2.4
$CaCl_2$	6.7	1.2	28.0	6.9
$AlCl_3$	1440 [b]	---	900 [b]	---

a. The time range over which the initial kinetic constant was measured varied from sample to sample

b. Measured over first 15 min

Na^+, Mg^{2+}, Ca^{2+} *and Al^{3+}. LiCl significantly increased the degradation of sucrose, as shown* in Fig. 1, and no initial degradation or lag phase was apparent. LiCl was expected to enhance water structure and, therefore, stabilize the sucrose solution. However the low charge/ionic radius ratio of LiCl (1.5) may have limited this effect.

Salt/solute effects were more striking when pseudo-first order kinetics of initial degradation over the lag phase period, as measured by OR and IC-IPAD, were calculated (see Table and Fig. 1). Sucrose hydrolysis has been shown to be a function of the concentration of sucrose and water.[3,18,19] 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.[19]

IC-IPAD is an accurate technique to measure sucrose degradation because it measures actual sucrose, but it can be tedious to operate. In comparison, 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; this assumption was made, especially when no color changes were apparent. However, as

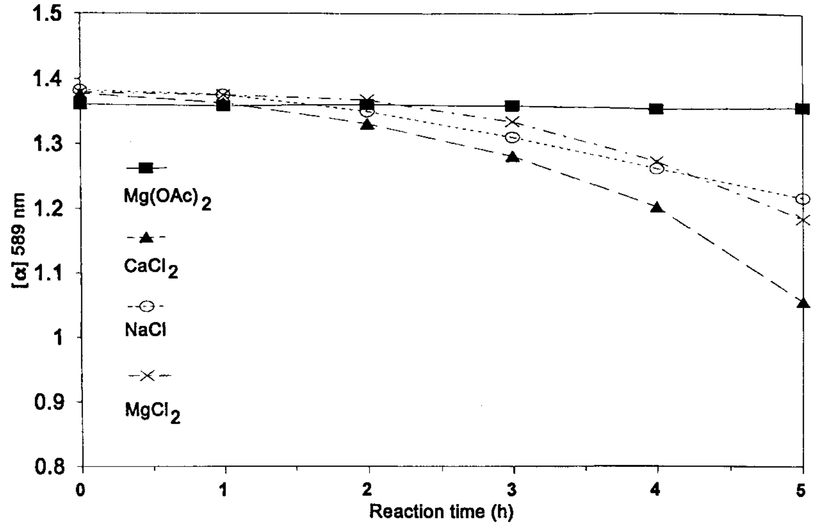

Fig. 2. Effect of various salts on the degradation of sucrose at 100 °C

can be seen in the Table, the rate values measured by OR were, in general, significantly lower than those calculated from IC-IPAD data (see also Fig. 1).

Similarly, Manley-Harris *et al.*[20] observed a small but significantly lower rate value for the alkaline degradation of a dilute 4% sucrose solution using OR compared to gas chromatography. This suggests that trace compounds with a high positive rotation may have been present. Another possibility was that salt complexation of sucrose caused an increase of the OR value on degradation; however, many workers[21] have shown that known sucrose-complexing salts usually decrease, rather than increase OR values, and a recent study in our laboratory with boric acid and sodium iodide (strong sucrose complexors[22,23]), confirmed no significant changes in OR of the unheated solution compared to the control (no salt added). The OR data may, therefore, have introduced an absolute error in the rate measurements, but the degradation pattern was generally the same for OR as IC-IPAD.

Effects of NaCl, $MgCl_2$ and $CaCl_2$ are illustrated in Fig. 2. All these salts shortened the initial lag phase with respect to the control, but the extent varied. $MgCl_2$ shortened the initial lag phase from ~4 h (as in the control) to ~2 h, and although the initial lag phase rate calculated from the OR data, was slightly lower than the control, the rate from the IC-IPAD data was higher (see Table). NaCl and $CaCl_2$ shortened the lag phase even further to ~1 h, and had slightly higher initial rates than $MgCl_2$ (Table). Furthermore, accelerated degradation, as seen in Fig. 2, was higher for the divalent cations. In contrast, Richards[5] (also working with 1:0.05 molar ratios of sucrose to salt, but with less water present, i.e., 7 mol water to 1 mol of sucrose) observed the addition of $MgCl_2$ effected a dramatic increase on accelerated degradation rate, as monitored by HPLC, with only a negligible lag phase. $CaCl_2$ and NaCl also affected the rate but to lesser extents than $MgCl_2$, with Ca^{2+} ions being more effective than Na^+ ions. The slightly higher sucrose concentration used by Richards[5] could have contributed to this discrepancy in results. However, as Richards[5] observed accelerated degradation in his pure sucrose control much earlier (~2 h) than we did, the Baker™ analytical sucrose used by Richards[5] may have had a higher indigenous salts content; our first studies, described above, showed that these varied considerably amongst lots of Baker™ analytical sucrose. Degradation rate increases in the presence of these neutral salts are difficult to explain with respect to enhanced water structure. The mechanisms proposed[5] for sucrose degradation are heterolytic, therefore, it may be possible that these salt effects occurred because of increases in dielectric constants of the sucrose model solutions.

$Mg(OAc)_2$ was observed to stabilize sucrose degradation (Fig. 2) over the reaction time studied (5 h). Similar stabilization was conferred by MgO, although not all the salt dissolved (results not shown). Milkova and Ivanov[24] reported that acid degradation of sucrose was inhibited by the alkali earth salts of weak organic acids because of their buffering capacity, and the effect was greater at 100 °C than 25 °C. Richards[5] reported that NaOAc conferred stability on sucrose and interpreted this as due to the neutralisation by the weak acetate buffer of secondary acidic degradation products which would form from any traces of primary hydrolysis products. Furthermore, $Mg(OAc)_2$ produced a weak alkaline solution which decreased in pH only slightly with reaction time, i.e., from pH 7.95 to 7.14, and MgO produced a strong alkaline solution which, within experimental error, changed negligibly in pH across reaction time, i.e., from pH 11.06 to 10.89. Sucrose is known to be relatively stable under alkaline conditions[2] because it lacks the unsubstituted hemiacetal grouping present in reducing disaccharides.

The addition of $AlCl_3$ had a remarkably different effect on sucrose degradation. The solution was highly acidic (initial pH 1.3) and acid degradation was extremely rapid (Table); a dark brown, viscous solution formed after 3 h. The changes in IC-IPAD chromatograms with reaction time are illustrated in Fig. 3 and show that sucrose was completely degraded after only 30 min. Moreover, reductones[25] were observed over the first 10 min of the subsequent chromatograms (Fig. 3), further indicative of severe acid degradation. Hydrated metal cations, if highly charged and small enough, e.g., Al^{3+} (charge/ionic radius = 6.7), can attract the unshared electron pairs of water molecules; the strength of attraction increases with charge of the ion and is strongest for the smallest cations. The process of

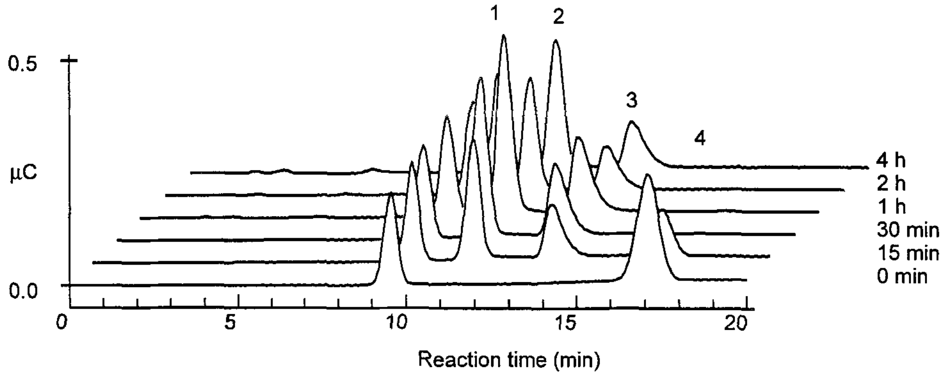

Fig. 3. IC-IPAD chromatograms[a] of effect of $AlCl_3$ on sucrose degradation at 100°C[b]
a. procedure described in EXPERIMENTAL section
b. peak identities: reductones at retention times less than 6 min, (1) glucosamine (internal standard), 9.5 min, (2) glucose, 11.2 min, (3) fructose, 14.2 min, (4) sucrose, 17.0 min

hydration is a Lewis acid-base interaction (metal cation acts as Lewis acid) and as a result of polarization water molecules bound to the metal ion are more acidic than those in the bulk solvent. The hydrated metal ion can thus act as a source of protons, as illustrated in Fig. 4.

The more polarized water molecules bound to the Al^{3+} ion (stronger Lewis acid) increase the tendency to transfer a proton to another electron donor, such as the glycosidic oxygen of sucrose. Overall, this can increase the concentration of the sucrose oxonium ion and sucrose acid degradation. Garber and Jones[26] previously observed that aluminium salts enhanced production of 5-hydroxymethylfurfural from acid catalyzed degradation of sucrose, glucose and fructose. This phenomenon may also explain the unexpectedly high accelerated rates of sucrose degradation in the presence of the divalent cations Mg^{2+} and Ca^{2+}, with charge/ionic radii of 3.1 and 2.1 respectively, especially as pH reduction was more marked than for the control (pH 6.25 to 3.54 and 7.29 to 3.5 for Mg^{2+} and Ca^{2+}, respectively) .

The second class of salts studied was larger ions, e.g., K^+ and Rb^+, which have weak attractive forces towards water and, therefore, act to reduce water structure. Both KCl and RbCl shortened the initial lag phase to ~1 h and slightly increased the initial degradation rate (Table). The drop in pH with reaction time, for KCl and RbCl, was slightly higher than the control, i.e., from pH 6.36 to 4.61 and pH 6.33 to 4.59 respectively, further indicative of increased degradation. Reduced water structure in the model systems may,

$$M(H_2O)_n^{z+} \rightleftharpoons M(H_2O)_{(n-1)}(OH)^{(z-1)+} + H^+ (aq)$$

Fig. 4. Interaction of water molecule with a cation of z+ charge.

therefore, have increased degradation by destabilizing the sucrose, although further verification with, e.g., NMR (nuclear magnetic resonance) studies, is required.

Fig.5 shows the reaction time dependence of OR for model sucrose systems in the presence of $MgBr_2$, MagnesiumCitrate ($C_6H_6O_7Mg$), $MgSO_4$, and $Mg(NO_3)_2$. The Hofmeister reactivity series of anions[13] follows the general order: citrate>sulfate>chloride>bromide>nitrate, but this order was not observed for sucrose degradation rates. For example, $MgSO_4$ was less effective than $Mg(NO_3)_2$ and $MgBr_2$ had little effect on sucrose degradation. The marked increase in degradation by $C_6H_6O_7Mg$ is undoubtedly because of the low initial pH (3.75) of the solution; however, it must be noted that in the context of sugar processing, carbonation (juice purification by adding $Ca(OH)_2$ and CO_2) removes practically all citrate ions. The Hofmeister series is proposed to relate to the ability of a particular ion to bind to a relatively hydrophobic site,[11,15] which consequently affects hydrophobic segment-solvent repulsive forces and the balance of intermolecular interactions which determine stability in solution. These results, therefore, indicate that direct binding of salts to hydrophobic sites on the sucrose molecule is not responsible, or is only partially responsible, in salt catalysed acid degradation. NO_3^- ions are considered to be strong water structure breakers, SO_4^{2-} less so,[10] and this may account for the effects of $MgSO_4$ and $Mg(NO_3)_2$ respectively. Another more simple explanation is that at 100 °C the ions of strong acids are formed, and sulfuric acid is a weaker, less volatile acid than nitric or hydrochloric acids.[27]

CONCLUSIONS

The tri-component system of sucrose-water-salt/solute, and its behavior at 100 °C, is intrinsically complex to analyse. Many points have been raised as to the possible mechanism of salt effects on the thermal degradation stability of the sucrose. There is no simple relationship evident to relate salt effect to thermal degradation of concentrated solutions of sucrose. However, some conclusions can be drawn from the results.

Highly charged, small cations significantly increase sucrose degradation through polarized hydrated ions/acidic pH effects. Larger cations, that act to reduce water

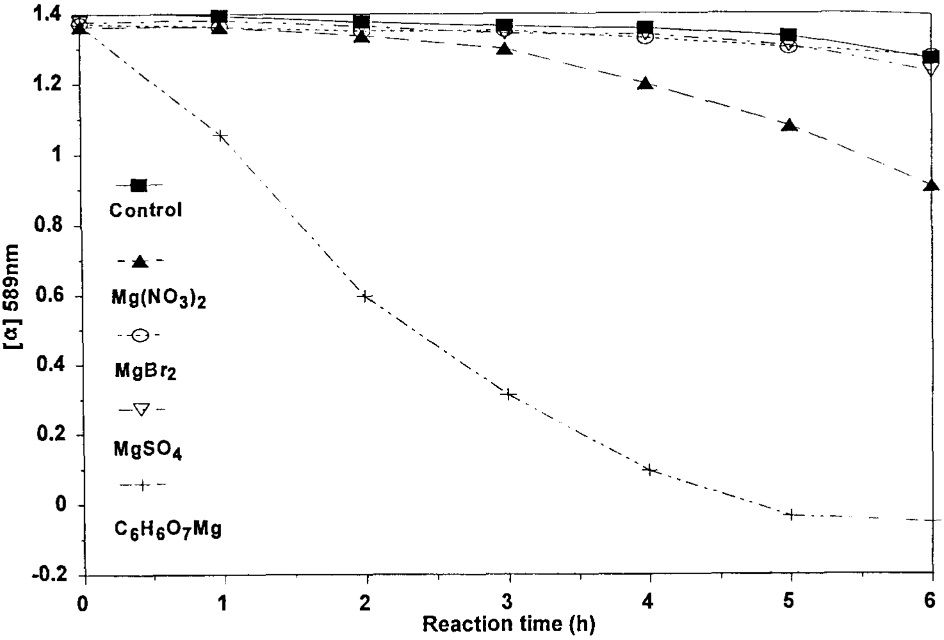

Fig. 5. Effect of Hofmeister anions on the degradation of sucrose at 100 °C

structure, increase degradation. Sucrose degradation effects do not follow the Hofmeister anion order, indicating that anion binding to hydrophobic or electrostatic sites on the sucrose molecule are not critical.

It is possible that the introduction of a salt/solute could affect the water around the sucrose not only by altering the bulk structure of water, but by displacing water from the sucrose hydration shell (preferential solvation) or altering the sucrose conformation, which in turn affects sucrose stability. Moreover, salts may affect the stability of sucrose in a way not related to effects on water structure. Direct salt-sucrose complexation and electrostatic effects may be involved.

Further studies to confirm salt versus pH effects, where the pH is kept constant over reaction time by using an automatic titrator, are presently in progress.

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). 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 the salt was dissolved into the solution. Portions (3 mL) of the reaction solutions were distributed in 5 mL Pierce Reactivials™, and sealed with Teflon septa. To avoid oxidative degradation of the substrates, the Reactivial tubes 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 and most salts were Baker analytical grade. Magnesium bromide, magnesium citrate (dibasic salt) and sodium borate were analytical grades from Aldrich, Sigma and MCB respectively.

Atomic Absorption Spectroscopy. Sucrose (10 g) was ashed in a muffle furnace at 525 °C, and then digested with nitric acid (5%). Cation concentrations were then measured on a Buck Scientific Model 200A atomic absorption spectrometer.

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 min.

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 (~25.0 °C). Results are expressed as specific rotations $[\alpha] = 100.\alpha / C.L$, 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 equipped with a quarternary gradient pump module (GPM). 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-equilibrate the column with the initial mobile phase prior to the next sample injection. Carbohydrates were detected using 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=+0.05 V (t_0=0.00 s), E_2=0.05 V

(t_1=0.42 s), E_3=+0.75 V (t_3=0.43 s), E_4=+0.75 V (t_4=0.60 s), E_5=-0.15 V (t_5=0.61 s), E_6= -0.15 V (t_6=0.96 s). The duration of the IPAD integration interval was set at 0.2-0.4 s. Using a Spectra-Physics SP8880 autoinjector and Dionex AI-450 chromatography software, runs were accumulated of 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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