Use of Differential Scanning Calorimetry and Thermogravimetric Analysis To Characterize the Thermal Degradation of Crystalline Sucrose and Dried Sucrose–Salt Residues

Gillian Eggleston,* Brenda J. Trask-Morrell, and John R. Vercellotti

Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, 1100 Robert E. Lee Boulevard, P.O. Box 19687, New Orleans, Louisiana 70179

Thermal degradation of pure sucrose in concentrated aqueous solution (100 °C, ~65 °Brix) in the presence of KCl, LiCl, NaI, and $Na_2B_4O_7$ was investigated. Polarimetry was used to quantify sucrose degradation, and pseudo-first-order kinetic constants of initial degradation rates were calculated. All salts significantly increased sucrose degradation; colored degradation products were only formed in the presence of $Na_2B_4O_7$. Thermal degradation characteristics of crystalline sucrose and dried, crystalline residues from sucrose–salt model solutions heated at 100 °C for 0 and 3 h were further investigated by differential scanning calorimetry (DSC), thermogravimetric (TG), and differential thermogravimetric (DTG) analyses. Rate of heating was 15 °C/min from 50 to 500 °C. DSC and TG studies confirmed the catalytic nature of salts on the thermal degradation of sucrose. Salts affected thermal degradation in various ways. The initial condensation degradation reactions were more rapid than expected, and subsequent elimination reactions were slower. The thermal analysis results indicate that complexation between the salt and sucrose is occurring, and further study at the molecular level is required.

INTRODUCTION

Impurities such as salts are known to increase the thermal degradation of concentrated sucrose solutions under industrial processing conditions, for example, in the sugar factory and refinery and in the manufacture of sugar-containing foods. This leads to chemical losses of sugar, reducing yields and unit process efficiencies. Consequently, not only are kinetic data required to better predict the kinetics of sugar losses, but also physicochemical and thermal data for engineers and designers are needed to make necessary process improvements. Recent studies by Eggleston et al. (1995, 1996) described the catalytic effects of various salts on the thermal degradation of concentrated aqueous solutions (~65 °Brix or percent dissolved solids) of sucrose, and initial degradation kinetic rates as monitored by optical rotation and ion chromatography were reported. However, the physicochemical behavior of sucrose under thermal conditions would be better defined using thermal analysis.

An understanding of the thermal or pyrolytic behavior of carbohydrate materials is important for many practical applications involving thermal processing operations such as clarification and evaporation unit processes in the sugar-processing industry and retorting, roasting, and baking in the food industry. Applications include the safe design of large-scale industrial trials (Biliaderis, 1990). Moreover, in sugar factories and refineries, sugar liquors are often subjected to 100 °C temperatures in, e.g., clarifiers, while localized heat spots can be much higher than 100 °C. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis have been widely used for determining physicochemical transformations occurring during the thermal degradation of carbohydrates (Biliaderis, 1990). These techniques measure net changes in enthalpy and weight as a result of many reactions taking place simultaneously and are particularly useful for indicating the temperature range and the rate of thermal processes as well as giving considerable information on physical and chemical changes. Furthermore, the carbohydrate content of foods is known to influence their thermal behavior (Biliaderis, 1990). Raemy and Loliger (1982) observed intense exothermic (DSC) reactions in heated foods of high carbohydrate content (>60%), e.g., maize, which are essentially because of the carbohydrate reactions.

Relatively little has been published on the thermal properties of sucrose, industrial brown sugars, syrups, and honeys and for the effects of salts and other food or process components even less. Richards and Shafizadeh (1978) investigated the thermal properties of pure, crystalline sucrose using TG and derivative TG (DTG) in a preliminary study to elucidate the mechanism of thermal degradation of sucrose. Haroun et al. (1976) investigated the thermal behavior of several unrefined Hungarian factory sugars using DTG analysis and observed that impurities such as ash and invertose (glucose and fructose) had a destabilizing effect on sucrose thermal properties. Maruyama et al. (1984) investigated the thermal characteristics of different honeys and high-fructose corn syrups (HFs) with TG and DTG. By TG and DTG rapid losses in the weights of fructose (F), glucose (G), and sucrose were observed in the ranges 200–300 and 500–600 °C, but thermal behavior in the range 200–300 °C varied with the sugar. In the TG and DTG curves of HF, weight loss in the range 200–300 °C depended on the F/G ratio. HFs with low F/G ratios (<1.28) predominantly reflected glucose thermal behavior, whereas HFs with high F/G ratios (>5) reflected fructose behavior.

This study uses model sucrose–salt systems to determine the kinetic constants of initial degradation rates of concentrated solutions of sucrose (~65 °Brix) at 100 °C. Salts studied included LiCl and KCl, water struc-
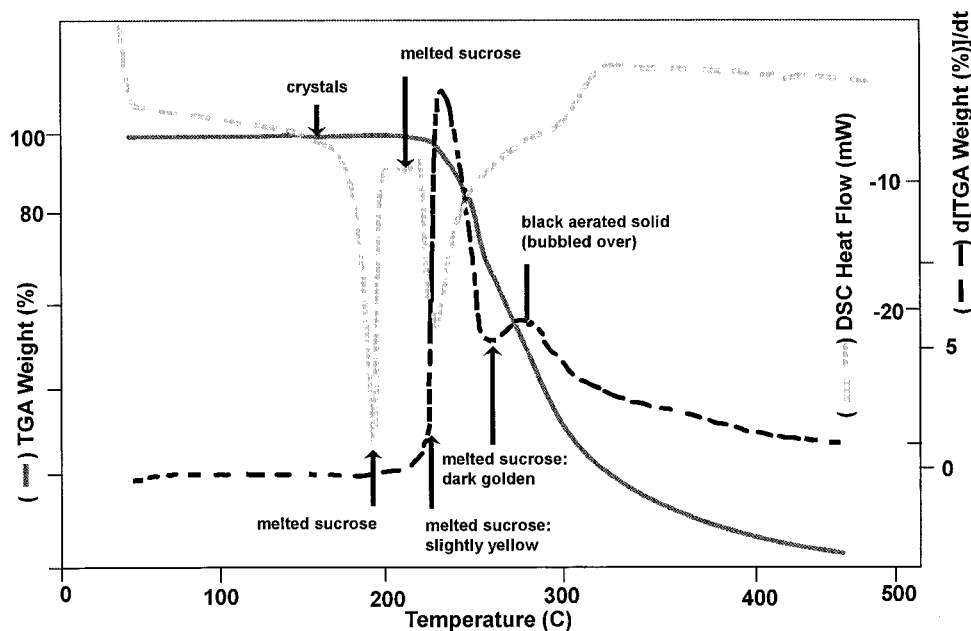
Figure 1. Overlaid thermogravimetric analysis (TGA), differential thermogravimetric (DTG), and differential scanning calorimetric (DSC) thermograms of pure, crystalline sucrose. Six selected final temperatures of analysis are indicated with the corresponding visual characterization of the resultant sucrose.

ture enhancer and breaker, respectively (see Eggleston et al., 1996), and $Na_2B_4O_7$ and NaI, salts known to complex with sucrose (Hernandez, 1963; Accorsi et al., 1989; Pollak and Mlynek, 1993) in order to further elucidate the mechanism of salt catalysis. In aqueous solution, metal cations are coordinated to water molecules. Hydroxyl groups of neutral carbohydrates can also coordinate to cations, but single hydroxyl groups cannot compete with the solvent; only a suitably arranged combination of two or three hydroxyl groups will result in significant (>1%) complex formation (Angyal, 1989). In the crystalline state, however, there being no, or only a few, solvent molecules present, hydroxyl groups of any carbohydrate may coordinate to any cation (Angyal, 1989). In order to more fully define the effect of salts on the thermal behavior of sucrose, select model solutions were carefully dried and investigated with DSC, TG, and DTG techniques.

MATERIALS AND METHODS

Reagents. Sucrose and most salts were Baker analytical grade. Sodium borate was analytical grade from MCB.

Analytical Procedures. *Sucrose Degradation Model Systems.* Model systems consisted of molar sucrose−water−salt/ solute ratios of 1:10:0.05, respectively (equivalent to a sucrose concentration of ~65 °Brix). Salt concentrations of 0.05 M were used because preliminary experiments had indicated significant and measurable degradations occurred at these concentrations. Waters of hydration of certain salts were taken into account when calculating the amount of water (resistance of 18 MΩ) 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 stored at −43 °C until analyses were undertaken.

Polarimetry. Samples were diluted with a weighed amount of water and their optical rotation (pol) measurements recorded at 589 nm, in a 10 cm path length 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 [α] = α100/*CL*, where α = measured rotation, *C* = concentration of sugar (g/100 mL of solution), and *L* = cell length (dm).

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

Sample Preparation for Thermal Analysis. Model sucrose− salt solutions at 0 (i.e., not heated) and 3 h reaction time were placed in a vacuum oven at 50 °C, overnight, until dried to constant weight. Crystalline salts were also dried.

Thermal Analysis. The thermal analyses were performed with a TA Instruments 2100 thermal analyzer. Differential scanning calorimetric (DSC) analyses were performed using a module equipped with a dual-sample cell and with autosampling capability. We used aluminum hermetically sealed pans to minimize detrimental effects of volatiles on the cell. The heating program was from 50 to 500 °C at 15 °C/min. Nitrogen was the purge gas and flowed at approximately 100 cc/min. Sucrose samples were weighed accurately and, if necessary, later normalized to 5.0 mg for comparability. TG analyses were made with the Automated Hi-Res TGA 2950 system. Samples were heated from 50 °C at 15 °C/min with a resolution setting of 3. This resolution setting most closely corresponds to the sensitivity of the older 920 module. Nitrogen purge gas was set according to manufacturer's guidelines at 40 mL/min flowing to the balance and 60 mL/min flowing to the furnace. Sucrose samples for TGA weighed 10−12 mg. The manufacturer's software programs were used to analyze and plot the thermal data. DSC and TG analysis packages, as well as curve overlay and file modification programs, were employed.

RESULTS AND DISCUSSION

Thermal Analysis of Crystalline Sucrose. The sequence of thermal degradation of crystalline sucrose was determined by DSC, TG, and DTG analyses as shown in Figure 1. The concurrent and consecutive individual reactions which take place within each thermal event are characterized by changes in mass (TG) and/or energy (DTG and DSC). Similar to observations by Richards and Shafizadeh (1978), Sopade et al. (1988), and Roos (1993), sucrose showed a sharp melting endotherm at ~188 °C, as monitored by DSC, which is followed by a slightly broader endotherm
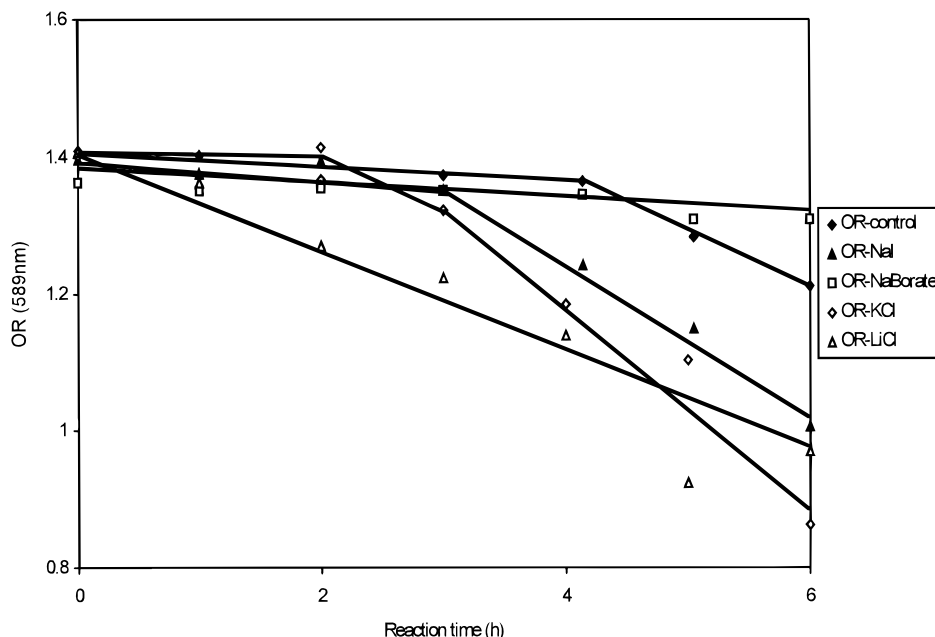
Thermal Degradation of Crystalline Sucrose

J. Agric. Food Chem., Vol. 44, No. 10, 1996 **3321**

Figure 2. Effect of salts on the degradation of concentrated sucrose solutions (65 °Brix) at 100 °C, as monitored by optical rotation (OR).

centered ~229 °C (see Figure 1). Finally, a broad exotherm was observed centered ~333 °C. However, it must be noted that the temperature of individual thermal events is dependent on the rate of heating. Although Richards and Shafizadeh (1978) did not report the exotherm, exothermic behavior was noted by Kelly and Brown (1978/79). As expected, no weight loss, as monitored by TG and DTG, occurred during the melting endotherm, but two subsequent major weight losses occurred with maximum and minimum rates of weight loss peaking at ~237 and 285 °C, which broadly correspond to the second DSC endotherm and the onset of the DSC exotherm, respectively. It is interesting to note that the second DTG weight loss peak was much smaller and less broad than that described by Richards and Shafizadeh (1978) despite the use of the same heating rate (15 °C/min), which may reflect the higher resolution capability of the newer thermal instrumentation. Another explanation could be that the starting materials differed, even though both were of analytical grade. The presence of trace amounts of salts, organic acids, or reducing sugars could have catalyzed degradation reactions and been responsible for the differences; furthermore, Eggleston et al. (1996) reported that trace salt cations vary among various analytical sucroses and even between lots of the same analytical sucrose.

Additional thermal runs were undertaken to assess the physical appearances of the sucrose at significant thermal steps. For example, a thermal sequence was run to the start and another to the end of the melting endotherm, and the sucrose was observed to be crystalline and melted, respectively. Results are indicated in Figure 1 and confirmed the individual thermal processes. Across the first and maximum DTG weight loss peak, the melted sucrose underwent degradation and subsequent color-forming reactions, with a slightly yellow color being discernible at the beginning and a dark golden product at the end of the peak, respectively. This colored sucrose melt then underwent strongly exothermic reactions (denoted by the DSC exotherm) to produce a black aerated charlike solid, which also signified that gas had been evolved during the exothermic reactions. The gas evolved is most likely a mixture

of gases including water (steam), carbon dioxide, and volatile products (Richards and Shafizadeh, 1978). Richards and Shafizadeh (1978) observed that the first weight loss peak represented condensation reactions leading to oligomeric and polymeric products, and they assumed the second weight loss peak represented "complex elimination reactions which yield solid char plus a wide range of volatile products".

Concentrated Sucrose−Salt Solution Model Systems: Thermal Degradation Characteristics. The degradation of concentrated aqueous solutions of sucrose (65 °Brix) in the presence of KCl, LiCl, NaI, and $Na_2B_4O_7$, as monitored by optical rotation (OR or pol), is illustrated in Figure 2. Very little sucrose degradation was observed in the model system containing only sucrose (control) over the first 4 h, with subsequent accelerated degradation from 4 to 6 h (see Figure 2). The initial lag phase is slow but finite. The first step in acid degradation of sucrose is protonation of the glycosidic oxygen (Richards, 1988) to form a sucrose oxonium ion, which undergoes a scission reaction to produce a fructose carbocation and glucose. The carbocation is lost by several reaction channels (Richards, 1988): It may add a hydroxyl ion from water to produce fructose, add to one of the hydroxyl oxygens of another saccharide (mostly sucrose) molecule to form oligosaccharides, undergo nonspecific degradation to a range of secondary products including organic acids and 5-(hydroxymethyl)furfural, or cyclize to form the anhydride. The initial trace amounts of organic acid secondary products formed induce the accelerated (autocatalytic) degradation curve (Figure 2) by further protonation of sucrose (Richards, 1988), and the ensuing organic acid formation is responsible for inducing the pH drop during the accelerated degradation reaction.

The effect of KCl and LiCl on sucrose degradation has been previously described by Eggleston et al. (1996), and the pseudo-first-order kinetic constants of initial degradation over the lag phase are listed in Table 1. Both LiCl and KCl, water structure enhancers and breakers, respectively, increased degradation (see Figure 2 and Table 1), with no color formation over 6 h reaction time. NaI did not markedly affect the initial degradation over

3322 *J. Agric. Food Chem.,* Vol. 44, No. 10, 1996

Eggleston et al.

Table 1. Effect of Salts on Degradation of Concentrated Sucrose Solutions

	initial pseudo-first-order kinetic constants at 100 °C[a]			
	polarimetry		IC-IPAD	
salt added (0.05 M)	k_1 (s^{-1} × 10^{-6})	SE (× 10^{-6})	k_1 (s^{-1} × 10^{-6})	SE (× 10^{-6})
control (no salt)[b]	2.6	0.3	3.8	1.0
potassium chloride (KCl)[b]	5.4	1.8	18.0	
lithium chloride (LiCl)[b]	20.0	0.3	69.0	26.0
sodium iodide (NaI)	3.1	0.5	ND[c]	
sodium borate (Na$_2$B$_4$O$_7$)	0.8	0.1	ND[c]	

[a] The time range over which the initial kinetic constant was measured varied from sample to sample. [b] Taken from Eggleston et al. (1996). [c] ND = not determined.

the first 2 h, but accelerated degradation was induced earlier than in the control; no color was formed. Although Na$_2$B$_4$O$_7$, as monitored by OR, did not appear to significantly affect degradation (Figure 2 and Table 1), a very pale color formed after only 1 h and the reaction solution was a very dark golden-brown color after 6 h, which signified that marked degradation had occurred. OR is widely used in the sugar-processing industry and is a very precise technique to measure sucrose degradation, provided that no other optically active compounds are present; this assumption was made, especially when no color changes were apparent. However, if traces of degradation compounds with a high positive OR are present, the OR kinetic change will be suppressed, and this is the likely explanation for the failure of OR to detect the degradation effected by Na$_2$B$_4$O$_7$. Furthermore, for model sucrose−salt solutions, Eggleston et al. (1995, 1996) calculated the pseudo-first-order kinetics of initial degradation over the lag phase period from OR and ion chromatography with integrated pulsed amperometric detection (IC-IPAD) data. IC-IPAD is a known sensitive technique for the specific measurement of sucrose. The kinetic values measured by OR were, in general, significantly lower than those calculated from IC-IPAD data (Eggleston et al., 1995, 1996; Table 1). This further suggests that traces of 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 degradation pattern was generally the same for OR as for IC-IPAD.

Differential Scanning Calorimetry. For thermal analysis the 0 and 3 h reacted model solutions were dried slowly under mild conditions, i.e., 50 °C, to prevent any further degradation prior to thermal analysis. The 3 h samples were investigated because degradation products formed over 3 h in aqueous solution further represent non-sucrose impurities in industrial sugar processing. Normalized DSC thermograms for the dried model solutions are illustrated in Figure 3. Both melting and reaction endotherms were similarly evident in all the samples. Mathlouthi et al. (1986) studied the differential thermograms of crystalline (C) and quenched melt (QM) sucrose; the latter was prepared by heating the sucrose at its melting temperature (~188 °C) and stabilizing the molten structure by rapid quenching. The QM sucrose was found to be completely amorphous as detected by X-ray diffraction (Mathlouthi et al., 1986) and showed a glassy transition at 60 °C and endothermic behavior which started at a lower temperature of 135 °C, rather than at the melting point of C sucrose. The endothermic behavior at slightly lower temperatures of the control dried sucrose solution (0 h reaction time) compared to the crystalline control can, therefore,
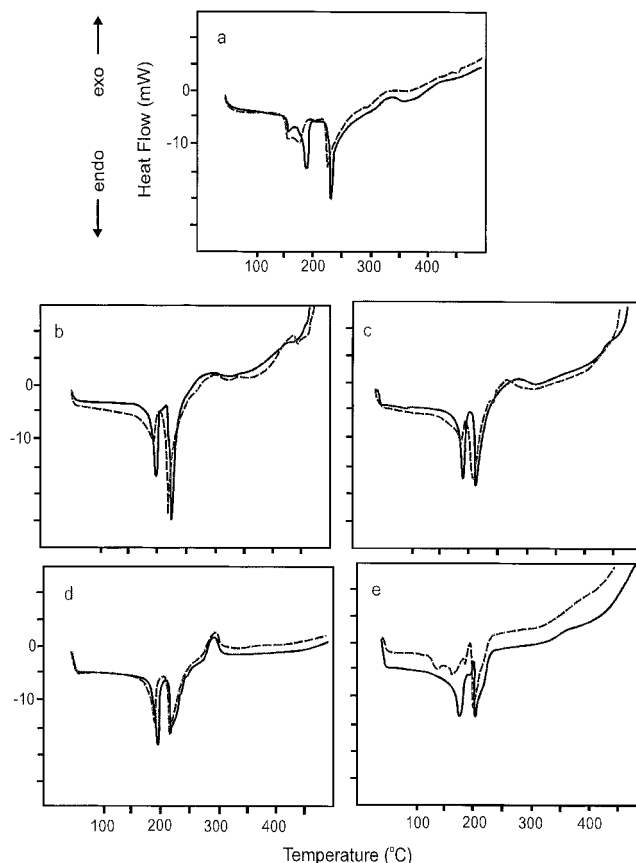

Figure 3. Overlaid DSC thermograms of dried residues of sucrose−salt. Thermograms of specimens representing reaction times of 0 h (solid line) and 3 h (dashed line) are shown. Sucrose (control, a) and residues of sucrose and (b) KCl, (c) LiCl, (d) NaI, and (e) Na$_2$B$_4$O$_7$ are illustrated.

be attributed to the slight production of amorphous sucrose on drying down the solution (see Figure 3a).

Although the normalized DSC thermograms of the model sucrose−salt samples at 0 h (Figure 3b−e) indicate the majority of the sucrose was in the crystalline state, the slightly reduced melting endotherm peak temperatures, from the crystalline melting endotherm of the control (see Figure 3a), may reflect small amounts of amorphous sucrose. However, a more likely explanation is that the salts thermally destabilized the sucrose to lower temperatures as melting endotherm peak temperatures of the 3 h dried samples were consistently shifted to even lower temperatures than the 0 h samples (Figure 3), which further suggests that thermal degradation of sucrose was facilitated in the presence of these salts, although there was a less marked reduction in enthalpy than in the 0 h samples. This facilitation could be attributable to the presence of catalytic degradation products formed over the 3 h reaction time of the model sucrose−salt solution (before drying) or to direct complexation of the salt and sucrose in the crystalline state. The unusual melting endotherms for Na$_2$B$_4$O$_7$ (Figure 3e) at 3 h may reflect the melting of the colored and noncolored degradation products already present in the sample (see previous section) and/or the presence of amorphous sucrose.

Thermogravimetric Analysis. DTG thermograms of the dried sucrose−salt residues are illustrated in Figure 4, and some thermal characteristics from the TG studies are listed in Tables 2 and 3. As for the DSC thermograms, the rates of weight loss peaks (maximum and minimum) were similar in shape to those of the
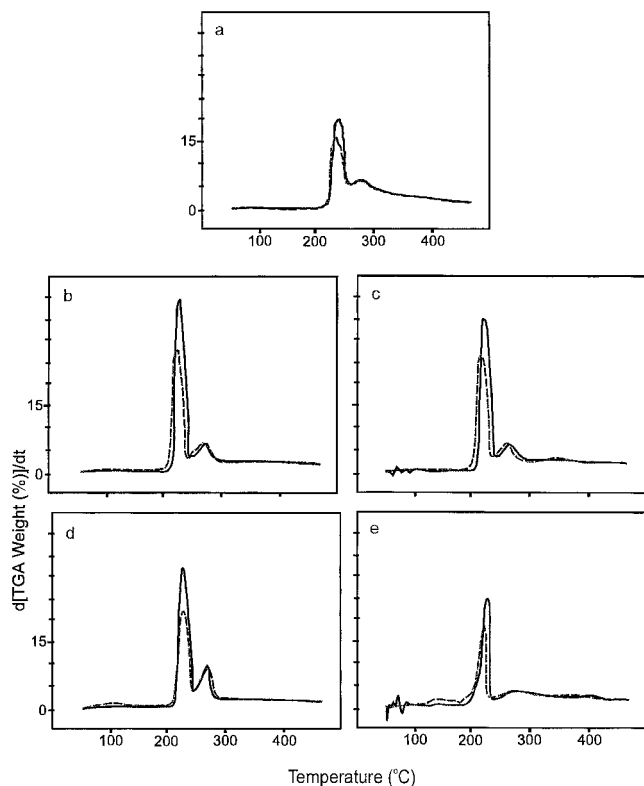
Thermal Degradation of Crystalline Sucrose

J. Agric. Food Chem., Vol. 44, No. 10, 1996 **3323**

Figure 4. Overlaid DTG thermograms of dried residues of sucrose–salt. Thermograms of specimens representing reaction times of 0 h (solid line) and 3 h (dashed line) are shown. Sucrose (control, a) and residues of sucrose and (b) KCl, (c) LiCl, (d) NaI, and (e) $Na_2B_4O_7$ are illustrated.

sucrose control, although the second (minimum) peak was less separated than in the control. Peak temperatures for the 0 h samples were all markedly shifted to lower temperatures than the control and those for the 3 h samples to a further extent, which confirms the DSC evidence that salts and sucrose thermal degradation products, respectively, destabilize sucrose and facilitate its thermal degradation (see Figure 4 and Table 2). Haroun et al. (1976), in a DTG study of pure crystalline sucrose and several unrefined (brown) factory sugars, observed that the factory sugars with relatively high ash contents ($\sim$1.3–2.0%) had endotherm peak temperatures shifted to lower temperatures than the pure sucrose peak. Furthermore, a factory sugar with relatively high ash (1.3%), moisture (3.0%), and invertose (0.2%) contents had the lowest endotherm temperatures, which endorses the assertion of the thermally destabilizing effect of sugar impurities.

The rates of weight loss values for the maximum peaks (R_{max}) of all the sucrose–salt samples were higher than for the control (Table 2). Rate is an indicator of how easily the thermal process is occurring, and the higher values further reflect the facilitation of the sucrose thermal processes by the presence of the salts. The rates at the inflection point between the two peaks for the sucrose–salt samples were lower than for the control, which confirms that the thermal processes represented by the two peaks were more widely separated entities. From 0 to 3 h R_{max} decreased for all samples (Table 2 and Figure 4), and this effect was strongest in the sucrose–salt samples. The degradation products already present in the samples most likely created a more viscous "reaction syrup" which caused a slower rate. In general, the minimum peak rates (R_{min}s) did not vary significantly from 0 to 3 h, which suggests

that impurities from sucrose degradation have more effect on the condensation reactions prevalent in the first (maximum) peak. R_{min}s in the presence of LiCl and KCl were broadly similar to the control values, whereas for NaI and $Na_2B_4O_7$, R_{min}s were higher and lower, respectively (Table 2).

Weight losses calculated from 170 °C to the inflection point (denoted by A) and from the inflection to 400 °C (B) are listed in Table 3. With the exception of the sucrose–NaI sample, the weight losses were greater in interval A for the sucrose–salt 0 h samples, whereas the loss was greater in interval B for the 0 h control; this is even more evident from comparing the ratios of A:B (Table 3). This further suggests that salt effects are more pronounced in the first initial condensation reactions (maximum peak). Moreover, this is further evident in the 3 h sucrose–$Na_2B_4O_7$ sample, qualitatively known to contain the most degradation compounds because of its golden-yellow color, which had markedly less weight loss in interval B. In general, from 0 to 3 h, weight loss in interval A decreased slightly for all samples, which reflects the decreasing R_{max} values. In contrast, for interval B, weight loss increased slightly from 0 to 3 h, especially in the control, which generally reflects the increasing R_{min} values.

By simple addition of the individual percent total weight losses for the crystalline salts and sucrose (control), taking into account the exact weight proportions of salt and sucrose in each model solution, it was possible to calculate the "expected" or "theoretical" percent overall total weight loss from the sucrose–salt (0 h) dried solutions. The expected losses are listed in Table 4. Expected losses of the 3 h solutions were not calculated, as the exact amounts of sucrose present were not known due to the formation of small amounts of degradation products in solution. As can be seen in Tables 3 and 4, for all the sucrose–salt solutions at 0 h, the observed percent total weight loss was always significantly lower than the expected value, which is strongly indicative of the formation of a stronger complex that reduces the overall amount of pyrolysis of sucrose under these crystalline conditions. From Tables 3 and 4 it was also observed that the dried 0 h control solution also had slightly lower observed losses than expected losses, and this must be because of the presence of slight amounts of amorphous sucrose, which confirms the DSC results. However, the observed losses of the 0 h sucrose–salt samples were still significantly lower than the 0 h control value, which eliminates amorphous sucrose being solely responsible. In case any residual moisture in the dried samples may have been totally or partially responsible for the lower observed values, we undertook similar theoretical calculations using data from interval B (inflection to 400 °C) and the interval 170–400 °C (after water is eliminated), which are also listed in Table 4, and similar relationships were found. Furthermore, the lower observed values are mostly due to the lower minimum peak weight loss values (B), as the observed weight losses across the maximum peaks (A) were actually higher in sucrose–salt samples (Table 3). The expected percent total weight loss values for KCl and LiCl at 0 h lie within the range of values for the known strong complexors of sucrose in solution NaI and $Na_2B_4O_7$ (Hernandez, 1963; Accorsi et al., 1989; Pollak and Mlynek, 1993), and the difference between the observed and expected percent weight loss values was highest for KCl. Although salts are known (Angyal, 1989) to form

3324 *J. Agric. Food Chem.,* Vol. 44, No. 10, 1996

Eggleston et al.

Table 2. Some TGA Characteristics of Sucrose−Salt Residues[a]

sample	reaction time (h)	rate (%/min)			temperature (°C)		
		max peak	min peak	at inflection	max peak	min peak	at inflection
crystalline sucrose		17.6 ± 0.6	6.8 ± 0.0	5.5 ± 0.6	237.4 ± 0.9	284.9 ± 3.4	265.6 ± 3.4
sucrose (control)	0	19.4 ± 1.3	6.5 ± 0.2	5.3 ± 0.2	240.4 ± 0.0	283.1 ± 4.3	264.4 ± 1.7
sucrose (control)	3	16.7 ± 1.2	7.0 ± 0.2	5.5 ± 0.4	233.2 ± 3.4	280.1 ± 8.5	259.0 ± 4.3
crystalline KCl		NA[b]	NA	NA	NA	NA	NA
KCl	0	38.7 ± 3.6	6.5 ± 0.1	3.4 ± 0.2	224.2 ± 0.9	268.0 ± 0.0	245.2 ± 0.0
KCl	3	30.1 ± 2.1	7.1 ± 0.4	3.3 ± 0.0	223.0 ± 4.3	268.0 ± 3.4	240.4 ± 5.1
crystalline LiCl		NA	NA	NA	NA	NA	NA
LiCl	0	36.6 ± 1.2	6.4 ± 0.1	2.7 ± 1.1	221.8 ± 0.9	266.2 ± 0.9	247.2 ± 5.7
LiCl	3	26.8 ± 0.5	6.4 ± 0.3	3.4 ± 0.3	219.4 ± 2.6	256.6 ± 2.6	237.2 ± 2.7
crystalline NaI		20.4 ± 5.4	7.3 ± 0.2	1.0 ± 0.0	144.2 ± 5.1	75.1 ± 7.7	87.1 ± 4.3
NaI	0	32.4 ± 0.6	9.2 ± 0.5	4.1 ± 0.1	227.2 ± 3.4	268.6 ± 4.2	245.2 ± 5.1
NaI	3	23.4 ± 0.9	9.3 ± 0.1	3.6 ± 0.1	224.2 ± 2.6	268.6 ± 2.6	240.4 ± 1.7
crystalline $Na_2B_4O_7$[c]		2.81	2.81	2.43	116.69	134.62	129.81
$Na_2B_4O_7$[c]	0	25.43	3.78	1.97	223.56	280.05	237.98
$Na_2B_4O_7$[c]	3	19.09	3.61	2.19	218.75	270.43	230.77

[a] Average of duplicates ± standard error. [b] NA = not applicable. [c] One replicate only.

Table 3. TGA Observed Weight Loss Characteristics of Sucrose−Salt Residues[a,b]

sample	reaction time (h)	weight loss (wt %)			ratio of A:B	total wt loss (wt %)
		A (170 °C to inflection)	B (inflection to 400 °C)	170−400 °C		
crystalline sucrose		29.5 ± 3.0	43.2 ± 0.9	71.2 ± 1.4	0.68	75.6 ± 2.0
sucrose (control)	0	33.2 ± 0.8	38.2 ± 0.5	70.4 ± 1.6	0.87	75.5 ± 1.6
sucrose (control)	3	29.2 ± 2.7	44.8 ± 0.7	73.2 ± 3.8	0.65	78.5 ± 6.0
crystalline KCl		NA[c]	NA	NA	NA	23.9 ± 4.3
KCl	0	36.2 ± 1.4	27.6 ± 1.2	61.0 ± 2.3	1.31	65.6 ± 2.6
KCl	3	35.6 ± 3.2	34.3 ± 2.5	71.0 ± 5.1	1.04	71.8 ± 4.4
crystalline LiCl		NA	NA	NA	NA	71.8 ± 0.0
LiCl	0	35.8 ± 0.2	28.2 ± 2.6	62.3 ± 0.7	1.27	67.9 ± 0.9
LiCl	3	31.7 ± 0.8	30.2 ± 0.1	59.2 ± 0.7	1.05	65.0 ± 0.9
crystalline NaI		NA	NA	NA	NA	42.0 ± 3.0
NaI	0	31.4 ± 1.4	36.6 ± 1.3	66.3 ± 2.7	0.86	70.2 ± 2.9
NaI	3	27.2 ± 2.1	39.2 ± 1.1	65.1 ± 0.4	0.70	70.5 ± 0.1
crystalline $Na_2B_4O_7$[d]		2.71	14.32	17.18	NA	19.10
$Na_2B_4O_7$[d]	0	33.61	21.81	55.14	1.54	66.42
$Na_2B_4O_7$[d]	3	31.81	23.44	54.92	1.36	62.75

[a] Average of duplicates ± standard error. [b] For expected weight losses, see Table 4. [c] NA = not applicable. [d] One replicate only.

Table 4. Expected (Calculated) Percent Weight Losses of 0 h[a] Dried Salt−Sucrose Residues, As Determined by TGA[b]

sample	reaction time (h)	expected weight loss (wt %)			
		A (170 °C to inflection)	B (inflection to 400 °C)	170−400 °C	total
sucrose (control)	0	29.5	43.2	71.2	75.6
KCl	0	29.2	42.8	70.4	75
LiCl	0	28.6	43	70.7	75.6
NaI	0	29.2	42.3	69.6	74.9
$Na_2B_4O_7$	0	28.7	42.4	69.6	73.9

[a] 3 h samples not determined (see text). [b] Corresponding observed values can be seen in Table 3.

complexes more readily with carbohydrates in the crystalline state as studied here, and extrapolation from the crystalline to solution form is questionable, it is still likely that the increased degradation of sucrose in concentrated aqueous solutions in the presence of KCl and LiCl is caused by direct complexing of the salts with sucrose.

CONCLUSIONS

The thermal analysis methods utilized in this study measured physicochemical changes of crystalline sucrose and of dried, crystalline residues of sucrose−salt model solutions. DSC and DTG studies confirmed the catalytic nature of salts on the thermal degradation of sucrose. Salts greatly affected the initial condensation degradation reactions by increasing the expected rates and extents of degradation. This most likely created a more viscous "reaction syrup" causing rates and extents of degradation in the subsequent elimination reactions to be lower than expected. On comparison of observed total percent weight loss (from DTG analysis) with calculated or theoretical weight losses of 0 h samples, the observed value was always lower than the calculated value, and amorphous sucrose effects can be eliminated. This indicates that a complex between the sucrose molecule and salt, which loses less residue on thermal analysis than individual components, has formed in the crystalline state. However, the complex itself represents new material which is capable of thermally destabilizing the sucrose to lower temperatures than for sucrose alone. We believe complexation is occurring, and this needs to be further studied at the molecular level, for example, with the use of nuclear magnetic resonance (NMR) techniques.

The use of DSC and DTG, as reported here, may offer a quick, accurate, and routine technique to provide further knowledge of the chemical and physical characteristics of sucrose containing salts or other impurities, which are often encountered in the food- and sugar-processing industries, and may be of particular interest to industrial processing engineers.

Thermal Degradation of Crystalline Sucrose

J. Agric. Food Chem., Vol. 44, No. 10, 1996 **3325**

LITERATURE CITED

Accorsi, C. A.; Bertolasi, V.; Ferretti, V.; Gilli, G. The crystal structure of the adduct 3NaI.2Sucrose.3H₂O. *Carbohydr. Res.* **1989**, *191*, 91.

Andrushchenko, V. P.; Kashurin, A. N. Evaporative capacity of sugar-syrup solutions. *Izv. Vyssh. Uchebn. Zaved., Pishch. Tekhnol.* **1989**, *3*, 47–49.

Angyal, S. J. Complexes of metal cations with carbohydrates in solution. *Adv. Carbohydr. Chem.* **1989**, *47*, 1–43.

Biliaderis, C. G. Thermal Analysis of Food Carbohydrates. In *Thermal Analysis of Foods*; Harwalkar, V. R., Ma, C.-Y., Eds.; Elsevier: London, 1990; Chapter 7, pp 168–220.

Eggleston, G.; Vercellotti, J. R.; Edye, L. A.; Clarke, M. A. Behavior of Water Structure Enhancing and Breaking Solutes on the Degradation of Sucrose. *J. Carbohydr. Chem.* **1995**, *14*, 1035–1042.

Eggleston, G.; Vercellotti, J. R.; Edye, L. A.; Clarke, M. A. Effects of Salts on the Initial Thermal Degradation of Concentrated Aqueous Solutions of Sucrose. *J. Carbohydr. Chem.* **1996**, *15*, 81–94.

Haroun, J.; Khattab, F.; Lorant, B. Thermogravimetric and thermoanalytical investigations of sugar by means of derviatograph. *Z. Zuckerind.* **1976**, *26* (8), 536–537.

Hernandez, J. A. L. Determination of Sucrose in the impure products of the cane sugar manufacturing process by the action of boron salts. *Int. Sugar J.* **1963**, *65*, 46.

Kelly, F. H. C.; Brown, D. W. Thermal decomposition and colour formation in aqueous sucrose solutions. *Sugar Technol. Rev.* **1978/79**, *6*, 1–48.

Maruyama, T.; Kanematsu, H.; Niiya, I.; Aida, Y.; Ohnishi, M. Pyrolysis behaviour of honey and high-fructose-corn-syrup. *J. Jpn. Soc. Nutr. Food Sci.* **1984**, *37* (1), 98–102.

Mathlouthi, M.; Cholli, A. L.; Koenig, J. L. Spectroscopic study of the structure of sucrose in the amorphous state in aqueous solution. *Carbohydr. Res.* **1986**, *147*, 1–9.

Pollak, V.; Mlynek, J. Calorimetric study of the interactions of D-glucose, D-fructose, sucrose, and poly (vinyl alcohol) with borate ions. *Carbohydr. Res.* **1993**, *241*, 279–283.

Raemy, A.; Loliger, J. Thermal Behavior of Cereals Studied by Heat Flow Calorimetry. *Cereal Chem.* **1982**, *59*, 189–191.

Richards, G. N. In *Chemistry and Processing of Sugarbeet and Sugarcane*; Clarke, M. A., Godshall, M. A., Eds.; Elsevier: Amsterdam, 1988; p 253.

Richards, G. N.; Shafizadeh, F. Mechanism of Thermal Degradation of Sucrose. A Preliminary Study. *Aust. J. Chem.* **1978**, *31*, 1825–1832.

Roos, Y. Melting and glass transition of low molecular weight carbohydrates. *Carbohydr. Res.* **1993**, *238*, 39–48.

Sopade, P. A.; Kearsley, M. W.; Le Grys, G. A. Heat of melting of sucrose. *Int. Sugar J.* **1988**, *90*, 1070.