

Response to Comment on the Melting and Decomposition of Sugars

Our response to “Comment on the Melting and Decomposition of Sugars” by Roos et al.¹ is organized into three sections: (1) explanation of terminology used and possible misunderstanding of our conclusion, (2) additional points of clarification and discussion, and (3) an analytical solution to determining the cause of the loss of crystalline structure in sucrose when heat (temperature) is applied.

■ EXPLANATION OF TERMINOLOGY USED AND POSSIBLE MISUNDERSTANDING OF OUR CONCLUSION

The objective of our first two *JAFC* papers^{2,3} was to determine the cause of the heating rate dependence of the DSC onset temperature of melting ($T_{m\ onset}$) in sucrose, glucose, and fructose, previously reported in the literature and confirmed in our papers.

According to the definition of thermodynamic melting based on Wunderlich⁴ given as follows, $T_{m\ onset}$ should not be dependent on heating rate (within a reasonable heating rate range): **Thermodynamic** melting of a crystalline material occurs at a single, time-independent (i.e., heating rate independent) temperature, where the crystalline solid and corresponding liquid phases are in thermodynamic equilibrium, ($\Delta G = 0$) at a constant pressure, with no change in chemical composition.

On the basis of the thermal and chemical analysis results reported in our papers,^{2,3} the initial loss of crystalline structure in sucrose, glucose, and fructose is in violation of three aspects of the definition of **thermodynamic** melting: (1) $T_{m\ onset}$ is heating rate dependent, (2) loss of crystalline structure can occur at temperatures well below the literature-reported melting temperature (time–temperature process), and (3) thermal decomposition compounds (glucose, fructose, and HMF) are detected concomitantly with the onset of the loss of crystalline structure (chemical change). Occurrence of thermal decomposition prior to the melting process changes the chemical composition of the system, along with its thermodynamics, and is responsible for the observed violations of the definition of **thermodynamic** melting given above. On the basis of this evidence, we concluded that the initial loss of crystalline structure in these sugars is caused by thermal decomposition, not by **thermodynamic** melting. Our conclusion that thermal decomposition can occur prior to thermodynamic melting is supported by a number of statements to this effect in the literature, including, surprisingly, the following statement by Roos:⁵ “Organic materials, such as numerous carbohydrates and sugars, are sensitive to temperature and may undergo degradation at temperatures below their melting temperatures.”

As evidenced by a large number of statements in Roos et al.,¹ it appears that these authors may have misunderstood our conclusion to mean that the **only way** for these sugars to lose their crystalline structure is for each sugar molecule to experience thermal decomposition (intramolecular bond breaking), which was not our intention. As reported in Lee et al.,³ select decomposition components **and** sucrose were detected

by HPLC analysis after complete loss of crystalline structure (see Table 3 in Lee et al.³ and associated chemical compositions provided in the text; e.g., the sample heated to 192.7 °C contained 61.78% sucrose), showing that, in addition to the loss of crystalline structure via the start of thermal decomposition, sucrose molecules can transition from the crystalline state to the amorphous liquid state without each molecule experiencing thermal decomposition. The complete, detailed mechanism of the loss of crystalline structure via thermal decomposition, as well as the contribution of additional mechanisms (e.g., dissolution), and factors (e.g., impurities, pH, residual water) under isothermal and nonisothermal heating conditions, was beyond the scope of the Lee et al.^{2,3} papers and requires further investigation. It is unfortunate that numerous statements in Roos et al.¹ imply that the Lee et al.^{2,3} papers did give a specific thermal decomposition mechanism, which appears to be that thermal decomposition begins with sucrose molecules embedded in the crystal lattice and that thermal decomposition occurs in all sucrose molecules. As was already discussed above, not all sucrose molecules undergo thermal decomposition, and there are a number of other possible mechanisms, including, but not limited to, thermal decomposition of (1) amorphous sucrose on the crystal surface, (2) sucrose molecules involved in or located near crystal defects, and (3) sucrose molecules in the mother liquor inclusions within the sucrose crystals (thermal induced hydrolysis). Further research is also needed to assess the effects of other factors, such as residual water, pH, impurities, and solvent used during crystallization, on the thermal decomposition of sucrose. Providing a specific thermal decomposition mechanism was never the intention of the Lee et al.^{2,3} papers, a very important point that needs to be taken into account when reading the Roos et al.¹ comment paper.

In an effort to be very careful about the terminology we used in our papers, we avoided the use of the terms “melt” or “melting”, because we felt that those terms were directly connected to the definition and requirements of **thermodynamic** melting. Instead, we used the phrase “loss of crystalline structure”. The terms “melt” or “melting” could be used in conjunction with thermal decomposition, if these terms are used to mean the physical transition from the crystalline to the liquid state (i.e., loss of long-range structural order without decomposition), without needing to adhere to the definition of **thermodynamic** melting given above (i.e., heating rate independence, occurrence at a single temperature, no change in chemical composition).

To try to clarify any confusion caused by not using the terms “melt” or “melting” in our original papers, we have attempted to rephrase the summary of our research findings below, incorporating the term “melting” to mean loss of crystalline structure due to applied heat (temperature) resulting in intermolecular bond breaking, not **thermodynamic** melting.

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On the basis of our thermal and chemical analysis results, thermal decomposition (intramolecular bond breaking with subsequent production of thermal decomposition components) is the kinetic process responsible for initiating the heating rate dependent loss of crystalline structure (conversion from the crystalline to the amorphous state) observed in sucrose, glucose, and fructose and is likely followed by melting (intermolecular bond breaking) and/or dissolution, depending on the heating conditions employed. However, as shown in Lee et al.^{2,3} the loss of crystalline structure in these sugars does not adhere to the definition of **thermodynamic** melting given above. The observed endothermic DSC peak is the sum of the enthalpy due to loss of crystalline structure caused by intramolecular bond breaking (decomposition), melting, dissolution, and any heat of reaction due to other chemical reactions/changes from the decomposition process (which appears to be insignificant at the start of decomposition). Thermal decomposition, melting, and dissolution processes are affected by one another (e.g., thermal decomposition compounds can act as solvents for crystal dissolution and thermal decomposition often occurs more rapidly in the liquid state than in the crystalline state), the heating conditions employed, and a long list of other factors, including surface and residual water, mineral impurities, noncrystalline (amorphous) residues, pH, etc. If very fast DSC heating rates could be achieved, it should then be possible to reach the **thermodynamic** melting temperature before thermal decomposition of these sugars can begin. Our rapid-scan DSC paper⁶ demonstrated that reaching the **thermodynamic** melting temperature was achievable for fructose, but not for sucrose or glucose, with the rapid-scanning rates employed (50–2000 °C/min). In our last paper,⁷ we investigated the effect of the production of thermal decomposition components (degradants) by both isothermal and nonisothermal heating conditions on the glass transition parameters of amorphous sucrose produced by melt-quenching.

As mentioned previously, further research is needed to elucidate the mechanistic details of each of these thermal events (thermal decomposition, melting, dissolution) in the loss of crystalline structure in these sugars, as well as the role of each of the additional factors listed above, under both isothermal and nonisothermal conditions. Finally, as evidenced by the confusion in terminology described above, a theoretical framework for “melting” and a lexicon for describing the loss of crystalline structure via the kinetic process of thermal decomposition need to be harvested and developed for use in the food science literature. There is already a considerable amount of research available on the subject of solid-state reactions in other fields, specifically materials chemistry, materials science, and pharmacy (see, e.g., refs 8–10).

■ ADDITIONAL POINTS OF CLARIFICATION AND DISCUSSION

The following is a list of responses, in order of appearance, to individual points made in Roos et al.¹ A brief title for each response is provided to aid the reader in following the main idea of each clarification and discussion point.

Press Release. As discussed under Explanation of Terminology Used and Possible Misunderstanding of Our Conclusion, the sugars we studied do not adhere to the definition of **thermodynamic** melting; however, the loss of crystalline structure initiated by thermal decomposition is likely followed by melting and/or dissolution, where melting simply

means loss of crystalline structure by applied heat. The authors apologize for any confusion caused by the terminology used in press releases and associated popular press articles. This was not our intention.

Wide Variation in Sugar Melting Parameters. Roos et al.¹ state that the wide variation in sugar melting parameters is “well known and acceptable”. The wide variation is well-known; however, there are a number of researchers attempting to determine the underlying cause of the variation as detailed in Lee et al.,^{2,3} thus the variation is not acceptable, but rather merits investigation and resolution. The factors discussed by Lee et al.,² and mentioned in Roos et al.,¹ can affect the melting process; however, they do not provide a complete explanation for the heating rate dependency displayed by these sugars. Thus, the main objective of the Lee et al. papers^{2,3} was to investigate the cause of the heating rate dependency displayed by these sugars.

Sample Purification. Roos et al.¹ stated that the sugars used by Lee et al.² “were used without **any** purification”. The sugars we used were of analytical grade, purchased from Sigma-Aldrich, and used without **further** purification. These are highly purified sugars as detailed in the Supporting Information provided in Lee et al.^{2,3} In addition to Sigma sucrose, several other analytical and commercial grade sucrose samples, which have been tested in our laboratory, have also displayed heating rate dependency behavior (unpublished data).

Crystal Size. Roos et al.¹ imply that the difference in crystal size between the sugars is of importance to the conclusions of Lee et al.¹ However, the difference in crystal size between the sugars is of no consequence to the results or conclusions of Lee et al.,^{2,3} because the heating rate dependence for each sugar was studied independently and not in comparison to each other. A similar number of crystals of the same size and weight, and in the same type of pan, were compared within each sugar at different heating rates. Therefore, comparison of crystal size between the sugars is not of importance.

Water Located in Amorphous Layers on Crystal Surfaces. Roos et al.¹ state that the water in the samples is located in amorphous layers on crystal surfaces; however, they did not provide any evidence or at least reference(s) to support this statement. Thus, the statement is conjecture and, moreover, serves to take the focus off the main idea: whether thermal decomposition occurs before **thermodynamic** melting in these sugars and initiates the loss of crystalline structure. There are a number of tangential statements in Roos et al.,¹ such as this, that take the focus off the main idea and thus could be confusing to the reader. In either case, whether there are or are not amorphous layers containing water on the surface of the crystal is not the primary issue at hand. If there is amorphous sucrose and associated water on the surface of the crystals, it is possible that thermal decomposition begins with these sucrose molecules. As mentioned previously, our papers were not intended to study the mechanism of thermal decomposition, but rather to study the origin of the observed heating rate dependency of these sugars. Further study is needed to elucidate mechanistic details.

Weight Loss Supposition. Roos et al.¹ state “The use of hermetic pans by Lee et al.^{2–5} meant that practically no water was lost from samples at the lower experimental temperatures. Unfortunately, the weight of the samples after DSC experiments was not reported. Loss of sample mass would have indicated loss of water.”

As a point of clarification, it is standard practice in our laboratory to record the DSC sample pan weights before and after scanning. If weight loss is observed and interferes with the thermal behavior of the sample, a new sample is run and/or the thermal parameters are adjusted. Thus, the conjecture by Roos et al.¹ that “Loss of sample mass would have indicated loss of water” is incorrect and, thus, their subsequent arguments are not applicable. In addition, if water was lost, that would delay the onset of “melting,” not cause it to occur at lower temperatures at lower heating rates (see Analytical Solution To Determining the Cause of the Loss of Crystalline Structure in Sucrose When Heat (Temperature) Is Applied).

Effect of Residual or Produced Water. Roos et al.¹ state, “It appears that Lee et al.^{2–5} did not take into account the presence of residual water, or water produced by decomposition of the sugars, in sample pans that were hermetically sealed. Even traces of water and smaller sugars as impurities in sucrose can start a progressive melting/dissolution process, followed by partial decomposition of the sugar.”

As mentioned under Explanation of Terminology Used and Possible Misunderstanding of Our Conclusion of this response paper, there are a number of factors that affect the thermal decomposition, melting, and dissolution processes, including residual water and impurities. If traces of water and smaller sugars as impurities in sucrose can start “progressive melting/dissolution,” without decomposition occurring first, then this same behavior should have been observed in mannitol, because mannitol had the highest water content and contained sorbitol as a measurable impurity in the “as-is” sample, as reported in Lee et al.³ However, mannitol’s melting parameters did not exhibit heating rate dependency, indicating that mannitol undergoes **thermodynamic** melting.

Finally, in a number of places in the text, Roos et al.¹ introduce and use the undefined terms “melting/dissolution” or “dissolution/melting” to explain the loss of crystalline structure in sucrose. However, they do not define the meaning of these slash-joined terms (the slash is most commonly used as the word substitute for “or” which indicates a choice), terms that represent very different processes. Even if the slash-joined terms were defined, the terms would not be sufficient to explain the findings of Lee et al.^{2,3} because neither melting nor dissolution should result in the detection of decomposition products in the amorphous liquid. Also, if “melting/dissolution” does occur before thermal decomposition, why does the DSC onset temperature increase as heating rate is increased?

Water Evaporation Produces “a Large Endothermic Shift in Heat Content”. Roos et al.¹ state “These decomposition reactions produce water that can cause an increase in the heat capacity reported in modulated DSC (MDSC) measurements. (The heat of evaporation of water is enormous, and even loss of traces of water from sample pans produces a large endothermic shift in heat content).”

This statement is based on the conjecture that the observed thermal effects were due to water being lost from the hermetically sealed pans. As previously stated, samples are rerun and/or conditions adjusted if weight loss affects the DSC results. Thus, these statements are incorrect. In addition, three other points should be made: (1) If evaporation did occur, there would be a decrease in mass, and therefore a decrease in heat capacity, but there was none. (2) Loss of even “traces of water” would cause a large “endothermic shift” in the data, but there was none. Heat capacity increases in a smooth, continuous manner as the crystalline structure becomes

amorphous. The heat of evaporation is a latent heat, not heat capacity. (3) An “enormous” amount of heat would affect the sample’s temperature, but the figure showed no such event. The measured sample temperature is plotted to show how temperature is changing with time.

Crystals, Instead of Melting, Dissolved Time-Dependently. Roos et al.¹ state “Lee et al.² need to correct their conclusion to note that the crystals, instead of melting, dissolved time-dependently in an increasing quantity of decomposition products and water that formed as a result of the partial decomposition of the amorphous sucrose phase.”

First, Roos et al.¹ make the assumption that the crystalline sucrose used contains an amorphous sucrose phase without providing experimental evidence and/or literature references. Amorphous sucrose may be present, but to prove this requires additional experiments. Second, in our *JAF*C papers, we make no claims about the mechanism for the start of thermal decomposition. Therefore, if Roos et al.¹ believe that the crystals “dissolved time-dependently in an increasing quantity of decomposition products and water that formed as a result of the partial decomposition of the amorphous sucrose phase”, then they are actually supporting our position that the loss of crystalline structure is the result of the onset of thermal decomposition. Finally, Roos et al.¹ make a contradictive statement to their previous comment when they say “This is very similar, conceptually, to the melting point depression of ice in frozen foods and can be related to the colligative properties and thermodynamics of solutions.” The melting of ice in a frozen solution is a thermodynamic process, which means that it is not time-dependent. Therefore, this is not conceptually similar to the melting of a frozen solute–water system.

Nature of the Endothermic DSC Peak. Roos et al.¹ make the following statement: “Lee et al.³ referred to Lee et al.² and stated that “These results prove not only that the loss of crystalline structure in sucrose is caused by thermal decomposition, but also that it is achieved via a time-temperature combination process’.” This statement, however, does not explain the fact that all sugars in the Lee et al.² study also exhibited a melting endotherm for the sugar. This must mean that the loss of crystalline structure did not occur by decomposition, but rather that there was melting/dissolution and associated decomposition.”

The issue in this paragraph is the interpretation that the DSC endotherm can only be due to the **thermodynamic** melting of sugar, which is a misapplication of the First Law of Thermodynamics. As illustrated in Figure 2 of Lee et al.,² there is an absolute, thermodynamic difference in enthalpy between crystalline and amorphous structures, and this difference increases measurably with temperature. Regardless of what causes conversion from the crystalline to the amorphous state (e.g., **thermodynamic** melting, partial or complete thermal decomposition, melting, dissolution, etc.), there must be an endothermic peak that reflects the absolute difference in enthalpy between the two states, because energy cannot be created or destroyed. This is a big problem in the literature because, in general, endothermic peaks are routinely identified as “melting” endotherms even though a number of them do not meet the thermodynamic and chemical requirements for **thermodynamic** melting behavior, which has been done in the case of sugars. This is the reason we proposed a new term, “apparent melting,” to be used to distinguish between the loss of crystalline structure initiated by kinetic processes, rather than **thermodynamic** melting. If the terms

“apparent melting” or “anomalous melting”¹¹ are confusing, other terms could be used, such as “crystolysis”¹² or “decrystallization”¹³.

Visual Observation of Decomposition Products. Roos et al.¹ report that they did “not see decomposition products (caramelization) on crystal surfaces during heating,” but did “see decomposition in the liquid phase of molecules released from the crystals (Figure 2)”.

At the onset of thermal decomposition, decomposition products are not visually observable. For example, in Table 3 (column 1, sample temperature of 149.4 °C) in Lee et al.,³ thermal decomposition components cannot be seen in the image, but small amounts of decomposition components were detected by HPLC analysis (quantities reported in the text). Thus, the onset of thermal decomposition cannot be identified by visual observation, but rather requires chemical analysis. Therefore, it is not valid for Roos et al.¹ to use visual observation during hot-stage microscopy to determine if liquid phase formation occurred prior to the production of thermal decomposition products or not. Chemical analysis, such as that used in Lee et al.,³ is required.

In addition to needing chemical analysis to determine the onset of decomposition, we have three additional concerns regarding the hot-stage microscopy study. First is the use of varied heating conditions **within** the hot-stage microscopy experiment (i.e., different heating rates and isothermal holding times mixed together in a single experimental run), rather than carrying out a systematic heating rate study. Because the impetus for the Lee et al.^{2,3} studies was the heating rate dependency of the loss of crystalline structure, it seems that it would have been more informative for Roos et al.¹ to carry out individual experiments using different heating rates (e.g., 1 and 10 °C/min), rather than one study with a mix of heating rates and holding times. In addition, an isothermal experiment at a temperature well below the literature-reported melting temperature (e.g., 120 °C) would have been very useful to perform.

Second is the lack of clarity regarding the microscopy observations and resulting conclusions. For example, the legend of Figure 2 says that isothermal holding at 140 °C for 30 min showed “some disintegration and cracking of the crystal at amorphous/defect regions,” with no mention of the development of a liquid phase, whereas the text indicates that cracking at the crystal surface did not occur until after a liquid sucrose phase appeared. It is not clear at what temperature the liquid phase actually developed; however, either way (liquid phase development before or after the cracking) these findings support, rather than contest, the work of Lee et al.^{2,3} If the liquid phase did appear at 140 °C, then Roos et al.¹ are visually confirming the conclusions of Lee et al.² that loss of crystal structure commences well below the literature-reported melting point. If some disintegration and cracking of the crystal did occur at 140 °C before the appearance of the liquid phase, this corresponds with statements by Bawn¹⁴ in his chapter on thermal decomposition of organic solids and also supports the work of Lee et al.^{2,3} According to Bawn,¹⁴ production of decomposition product molecules in the solid phase without partial melting induces strains in the crystal, which are relieved by the formation of cracks.

Third is the lack of hot-stage microscopy of mannitol, because mannitol was used by Lee et al.^{2,3} as a thermodynamic melting comparison material.

Definition of Thermodynamic Melting. Roos et al.¹ define the thermodynamic melting point as “the temperature at

which no crystalline material can exist”, but did not provide a reference to support their definition. This definition is very different from the one given in Lee et al.^{2,3} and repeated in Explanation of Terminology Used and Possible Misunderstanding of Our Conclusion herein, which is based on that of Wunderlich.⁴ The definition based on that of Wunderlich⁴ is the commonly accepted definition of **thermodynamic** melting and was not held to by the sugars examined in Lee et al.^{2,3}

Lack of Alternative Explanation. Roos et al.¹ state “... the evidence does suggest that the sugar molecules below their thermodynamic melting temperature gained mobility because of their dissolution/melting.”

This statement supports our findings that loss of crystalline structure occurs below the literature-reported thermodynamic melting temperature. Roos et al.¹ did not offer an explanation for the cause of the “dissolution/melting” process, which they acknowledge occurs below the **thermodynamic** melting temperature. Our explanation is thermal decomposition. It would have been apt for Roos et al.¹ to offer an alternative explanation.

No Chemical Change Can Occur before Melting. Roos et al.¹ state “There could be no chemical change of the sugar molecules before they were released from the crystal structure, as also shown by us in Figure 2.”

First, as discussed previously, chemical change must be measured using chemical analysis techniques, not by microscopic observation. Second, thermal decomposition (chemical change) can occur before release from the crystal structure, as suggested by a number of authors (see, e.g., refs 5 and 14–16). It would be helpful for Roos et al.¹ to provide references to support their statement that “no chemical change of the sugar molecules, before they were released from the crystal structure,” which is contrary to the information provided in the above references, including those by Roos.^{5,15} The concept that “a crystal is a chemical graveyard” is outdated, as discussed by Friscic and Day.¹⁷ Third, as already mentioned numerous times, the complete, detailed mechanism of the loss of crystalline structure via thermal decomposition was not the intent of the Lee et al.^{2,3} papers and requires further investigation.

Progressive Decomposition. Roos et al.¹ state “This hypothesis included the presence of surface water, which means that there must have been dissolved sucrose, particularly at temperatures above 100 °C. In turn, this means that a portion of sucrose was mobile and available to initiate a progressive decomposition and increased dissolution/melting of sucrose with increasing temperature.”

As we have stated a number of times, we made no claims about the mechanism of decomposition. If Roos et al.¹ believe that there is “progressive decomposition” as a result of dissolved sucrose, then they are again supporting our position that the loss of crystalline structure in sucrose is the result of the onset of decomposition.

Time Required for Production of Decomposition Products under Isothermal Conditions Is Inaccurately Reported. Contrary to the statement in Roos et al.,¹ thermal decomposition products were measured in sucrose samples held at 120 °C for **only 50 min**,³ **NOT after >50 h**. **Complete** loss of crystal structure required >50 h at 120 °C, but select thermal decomposition components were detected after only 50 min at 120 °C. Given the inaccuracy of the reported time required for production of decomposition products, the remarks that follow this statement are not pertinent.

Caramelization Requirements. Caramelization has generally been thought of as a complex series of reactions occurring under high temperature conditions, that is, at temperatures greater than the literature-reported melting temperature of sucrose.¹⁸ Thus, what has not been known for centuries is that caramelization can be carried out well below the literature-reported melting temperature of sucrose, using a low-temperature–long-time approach.

Factors Affecting DSC Results. Roos et al.¹ state “Our experience supports and we recommend the use of different sample masses in all DSC studies, to separate sample size-independent instrumental artifacts.”

We agree that sample size can affect DSC results. Therefore, the sample size should be optimized prior to data collection, where the size should be large enough to represent the bulk properties of the material, but as small as possible to minimize thermal lag in the sample. During preliminary data collection, we optimized the sample size used for each experiment and subsequently reported the sample sizes used under Materials and Methods of each of our papers. It is concerning that Roos et al.¹ spent a great deal of effort discussing topics such as sample size, but did not perform (or mention performing in their experience) heating rate dependent experiments, which are so germane to the work about which they have extensively commented.

Thermal Decomposition Mechanism. As stated by Roos et al.,¹ “The only way that decomposition can be thought to cause loss of crystalline structure is if the presence of decomposition products accelerates the release of the sugar molecules from their crystals. This, however, requires a noncrystalline phase (molecules released from the crystals or pre-existing amorphous phase), before the decomposition reactions can start and produce decomposition products to further accelerate melting/dissolution.”⁷ This is proved by the images shown here in Figure 2.”

As previously discussed, the mechanism for thermal decomposition was beyond the scope of our initial papers. However, thermal decomposition most likely starts on the surface and/or in cracks and defects within the crystal, creating decomposition products that further accelerate the loss of crystalline structure. Also, as previously discussed, the onset of thermal decomposition cannot be determined by visual inspection of microscopic images such as those shown in Figure 2; rather, chemical analysis is required (as was carried out in Lee et al.³). Thermal decomposition products were detected after the sucrose sample was held for only 50 min at 120 °C, prior to any visually observable color change.

ANALYTICAL SOLUTION TO DETERMINING THE CAUSE OF THE LOSS OF CRYSTALLINE STRUCTURE IN SUCROSE WHEN HEAT (TEMPERATURE) IS APPLIED

The purpose of this section is to further address two underlying issues expressed in Roos et al.:¹ (1) their belief that sucrose exhibits thermodynamic melting at 185 °C, despite the evidence in our *JAFC* papers, as well as corresponding evidence in the literature, and (2) the presence of a “melting endotherm for the sugar” in the DSC scan. To address these issues, additional analytical data, using the same Sigma-Aldrich sucrose (catalogue no. S0389) as used in the *JAFC* papers, are presented herein that show conversion of all crystalline structure to an amorphous liquid without ever heating the

sample above 130 °C. This temperature was selected because it is well below the literature-reported melting temperature for sucrose (so according to the definition given under Explanation of Terminology Used and Possible Misunderstanding of Our Conclusion, thermodynamic melting should not occur) and TGA data (both heating at 10 °C/min and isothermal at 130 °C) show that weight loss due to thermal decomposition begins immediately at a temperature of 130 °C (thus, the time needed to clearly show thermal decomposition at 130 °C should be relatively short).

The TGA used for these studies was a TA Instruments model Q500 (New Castle, DE, USA). Temperature calibration was carried out using a Nickel Curie point standard at 10 °C/min for the heating rate experiments and at room temperature against a research-grade thermometer, which had been calibrated in an ice bath, for the isothermal experiments. The design of the TGA is unique in that it has the ability to sense sample temperature with the location of the thermocouple and the ability to use large sample sizes for increased sensitivity. A cross-section of the Q500 design is shown in Figure 1. The typical sample weight used in these experiments was 130–140 mg.

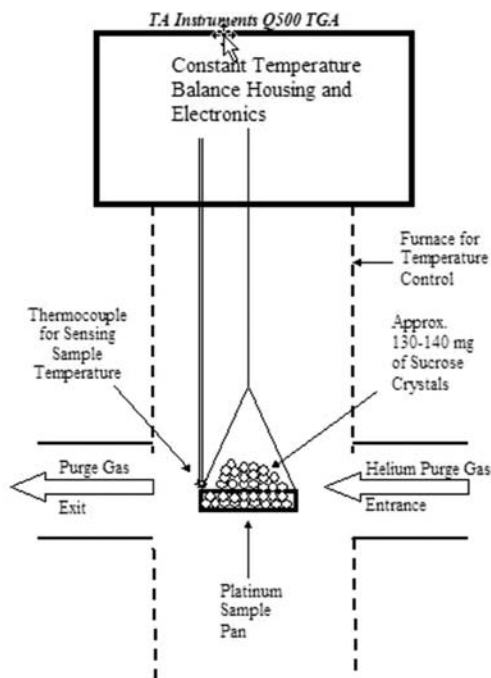


Figure 1. Cross-section of the TA Instruments Q500 design (New Castle, DE, USA).

Figure 2 displays data from a TGA experiment using a heating rate of 10 °C/min with helium purge gas for the furnace at a flow rate of 60 mL/min and nitrogen gas for the balance at a flow rate of 40 mL/min. The two weight curves are the exact same data, except that the baseline has been corrected for one set of data over the temperature range of 50–100 °C for easier visual interpretation of when weight loss begins. The most frequently reported temperature for the onset of weight loss is the “extrapolated” temperature, which is the temperature (155 °C) at which tangents to the baseline and transition region intersect. However, the data clearly show that weight loss begins at a temperature closer to 120 °C. As previously stated, these data were the basis of selecting 130 °C for the

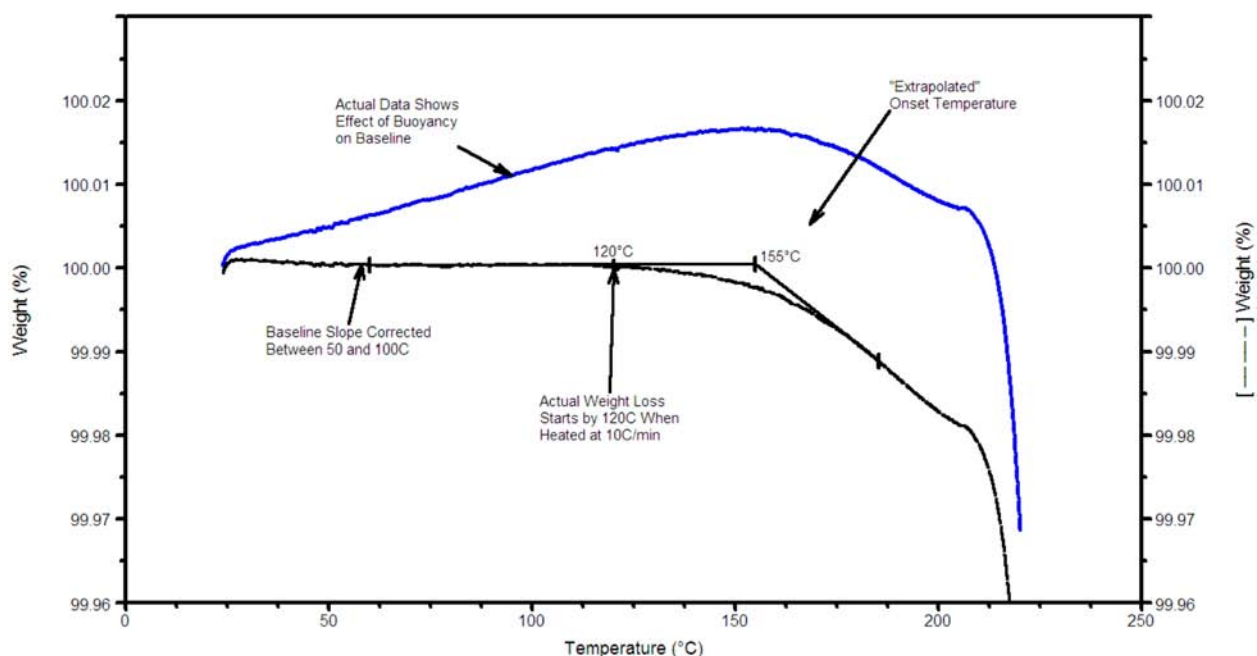


Figure 2. TGA weight loss experiment for crystalline sucrose at 10 °C/min.

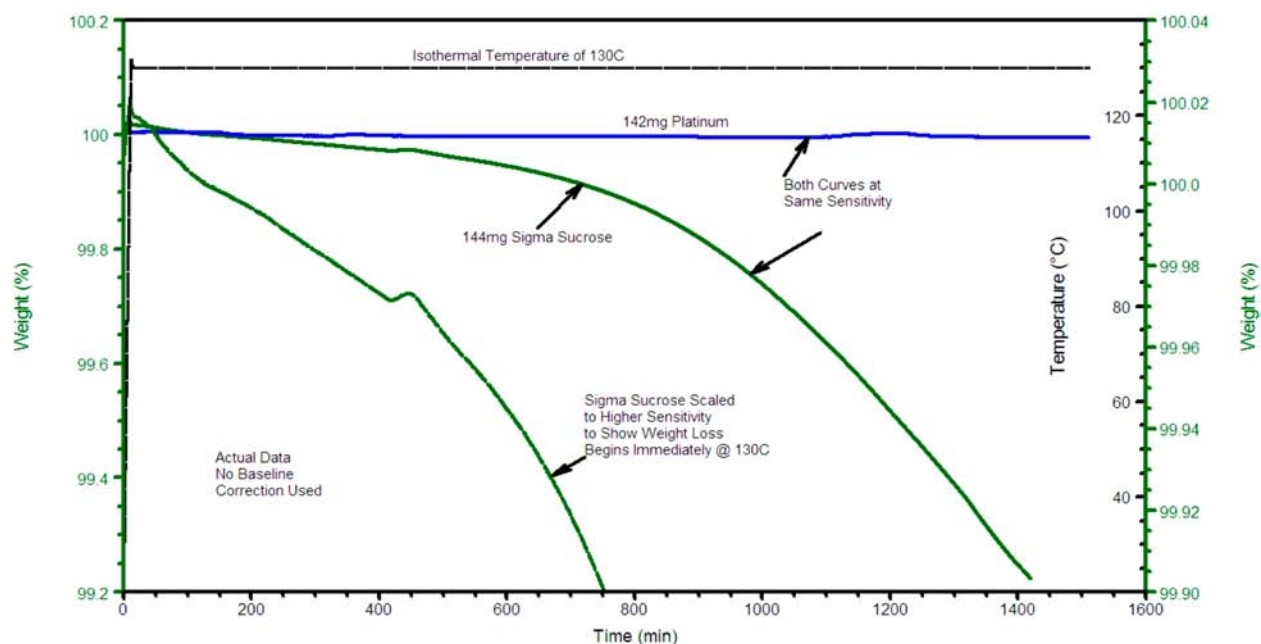


Figure 3. Isothermal TGA weight loss experiment for crystalline sucrose at 130 °C for 24 h.

isothermal experiment, which also confirms that weight loss begins immediately at 130 °C. It is important to note that there is no indication of measurable water loss from the sample before 120 °C.

A possible question is “Why is the weight loss so small if decomposition is occurring?” There are two answers to that question. First, weight loss due to thermal decomposition is zero at the start of decomposition. Second, when sucrose starts to decompose, the initial decomposition products are glucose and fructose carbocation (for details see the Sucrose Thermal Decomposition section in Lee et al.³). Neither of these materials is volatile at the decomposition temperature. Therefore, there cannot be a loss of weight. Only when there

are volatile decomposition products created, such as 5-(hydroxymethyl)furfural (5-HMF) (with a reported boiling point of 114–116 °C, Sigma-Aldrich MSDS¹⁹), can weight loss begin.

Figure 3 shows the change in weight of the sucrose sample in an isothermal TGA experiment at 130 °C over a 24 h time period. Nitrogen gas was used for both the furnace (60 mL/min) and balance (40 mL/min) purge gas. Because temperature is constant, except for the initial heating to 130 °C, there is no change in buoyancy and, therefore, no need to perform a baseline correction. However, because weight loss is only about 1%, a possible question may be about the stability of the TGA baseline over the time period of the experiment. For that

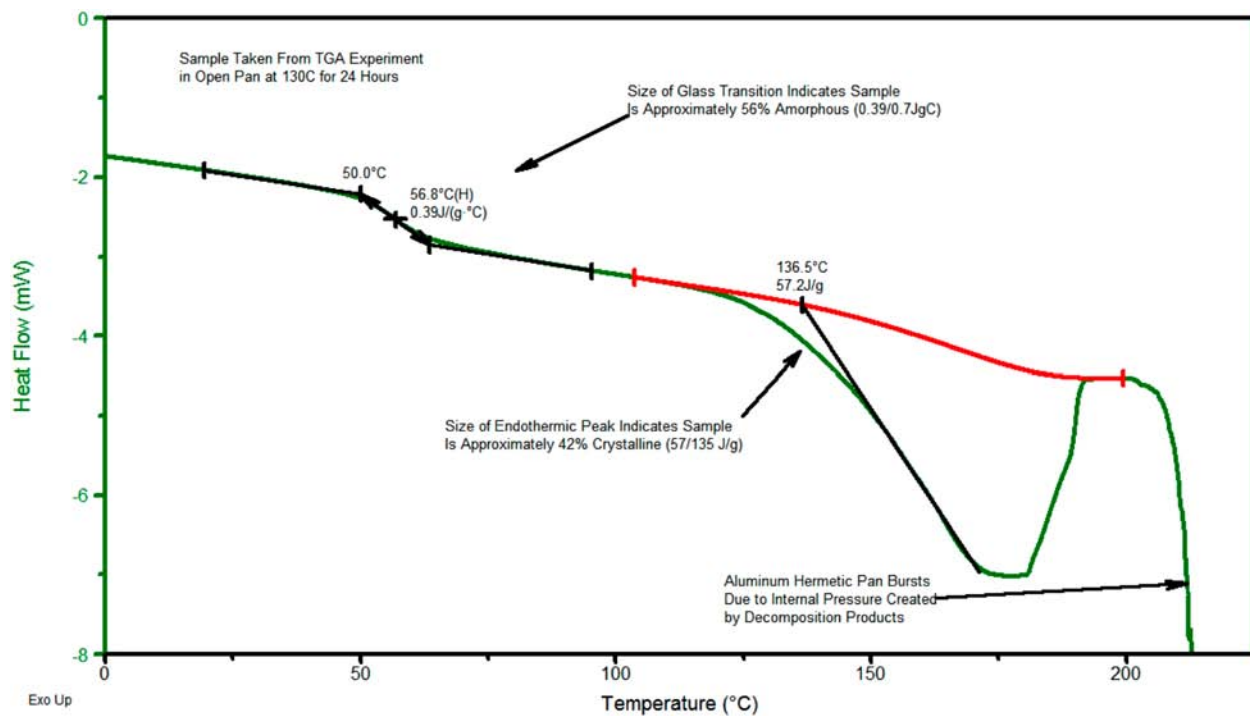


Figure 4. DSC scan of a sucrose sample that was held at 130 °C in the TGA for 24 h (TGA weight loss data shown in Figure 3).

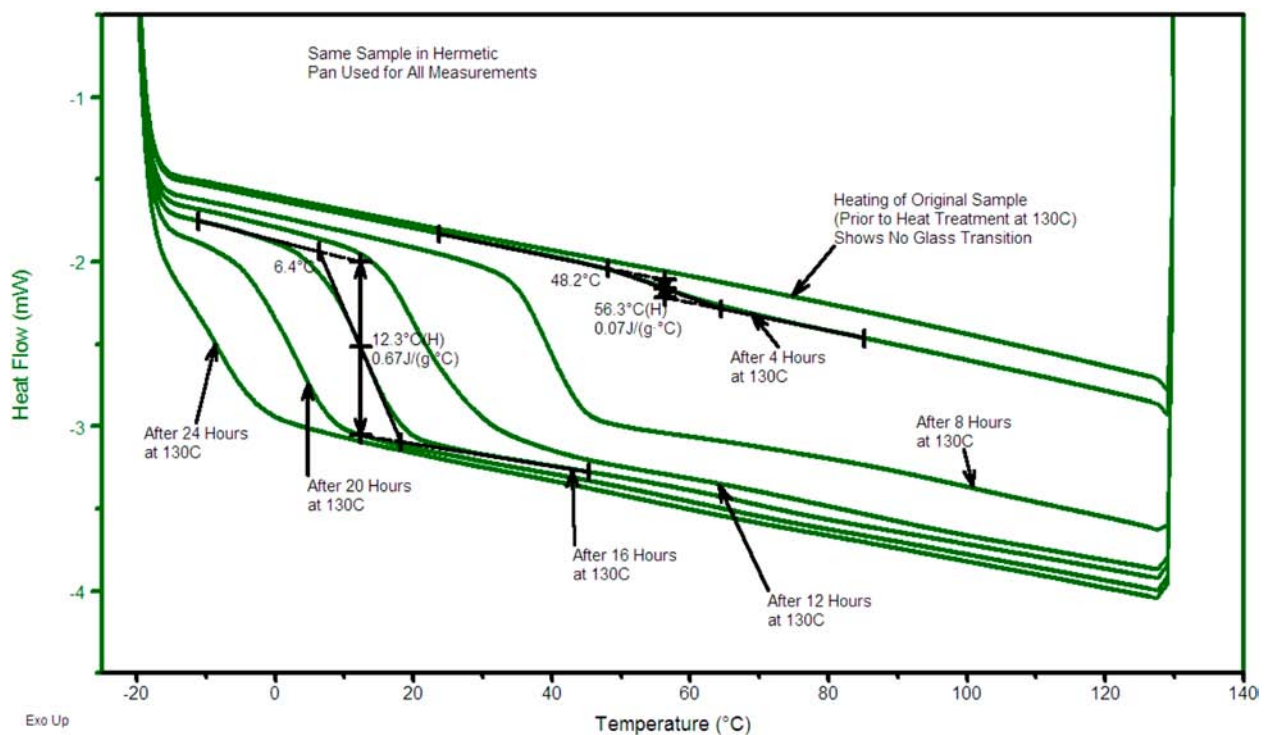


Figure 5. DSC scans of an "as-is" sucrose sample and after each of six 4 h isothermal periods at 130 °C.

reason, a 142 mg platinum sample was run under the same conditions to test baseline performance. As seen in the data, baseline performance was excellent and reliable. The sucrose data show that weight loss begins immediately at 130 °C, and the rate of weight loss increases after about 10 h.

It is important to consider that dry purge gas is flowing over the sample at a rate of 60 mL/min (see TGA design in Figure 1). This should result in volatile decomposition products being

quickly swept away from the sample and, therefore, unable to have a significant impact on the thermal decomposition process. At the end of the 24 h experimental time period, the following characteristics were noted about the sample: (1) The height of the pile of crystals had decreased by about one-third, and all crystals had fused together, indicating that molecular flow had occurred. (2) All crystals had a yellow color, but the intensity of the color varied between crystals. (3) At room

temperature, the yellow crystals were hard and brittle, indicating that their glass transition temperature was above room temperature.

In addition to the visible inspection of the 24 h sample from the TGA experiment, a DSC experiment was performed to determine how the structure of the initial crystalline sucrose sample had changed over time at 130 °C (Figure 4). A portion (9.81 mg) of the 24 h TGA sample was placed in a hermetically sealed DSC pan and heated at 10 °C/min from -20 to 225 °C in TA Instrument Q2000 DSC (New Castle, DE, USA), using a 50 mL/min nitrogen purge gas. The glass transition observed in Figure 4 is due to the mixture of amorphous materials produced during the thermal decomposition process. The size of the glass transition indicates that approximately 56% of the crystalline structure was lost due to the thermal decomposition process during the 24 h hold time at 130 °C. Again, it is important to recognize that volatile decomposition products should have been quickly swept away from the sample during the TGA experiment and therefore have only a minor effect on the loss of crystalline structure.

Although the TGA data show that thermal decomposition begins immediately and that the rate of weight loss increases with time at 130 °C, it does not show how the structure of the sucrose sample changes with time at that temperature. Therefore, a DSC experiment (TA Instruments Q2000 with 50 mL/min nitrogen purge) was performed in a hermetically sealed aluminum pan to measure how structure changes during the 24 h hold time at 130 °C. After each of six 4 h isothermal holding periods at 130 °C, the sample was rapidly cooled to -20 °C and then reheated at 10 °C/min back to 130 °C for an additional 4 h hold period. The reheating from -20 to 130 °C at 10 °C/min provided the desired information on structure, as shown in Figure 5. All thermal treatments occurred in the DSC cell, and the sample was not removed from the DSC cell during the entire experiment.

Because a hermetic pan was used, all decomposition products (volatile and nonvolatile) would remain in the pan over the 24 h time period of the experiment and have the potential to affect the crystalline to amorphous conversion rate. Results in Figure 5 show (1) there is no detectable glass transition in the "as-is" Sigma sucrose sample. This indicates very little, if any, amorphous structure in the original sample. (2) After as little as 4 h at 130 °C, approximately 10% of the crystalline structure has converted to the amorphous form. The calculation of approximately 10% is obtained by dividing the size of the glass transition (0.07 J/g·°C) by the size of the largest glass transition observed in the data (0.67 J/g·°C), which is within the range of values reported by Roos et al.¹⁵ for 100% amorphous structure of 0.60–0.77 J/g·°C. (3) Each 4 h period at 130 °C lowers the glass transition temperature by 10–20 °C. (4) After 24 h in a sealed pan at 130 °C, the onset temperature of the glass transition is below -20 °C. The decreasing glass transition temperatures in Figure 5 are due to the ongoing production and retention (because of the use of a hermetically sealed DSC pan) of amorphous thermal decomposition components (degradants) over the 24 h holding time at 130 °C. In addition, on the basis of the HPLC data reported in Lee et al.³ for the crystalline sucrose sample held at 120 °C, dissolution of sucrose by these thermal decomposition degradants is also likely. Because **thermodynamic** melting is not possible at 130 °C, we attribute the loss of crystalline structure to thermal decomposition and subsequent dissolution of sucrose in the sealed DSC pan.

In summary, the following conclusions can be drawn from the data presented in Figures 2–5:

1. The thermal decomposition of sucrose is shown to begin at least 50 °C below the often-reported melting temperature of 185 to 190 °C.
2. Thermal decomposition begins immediately at 130 °C and causes loss of approximately 10% of the crystalline structure within just 4 h.
3. The thermal decomposition products of glucose and fructose carbocation are not volatile and, therefore, the weight loss due to decomposition observed in the TGA data is very small.
4. The thermal decomposition process causes loss of crystalline structure. The rate of crystalline to amorphous conversion is much faster in sealed (Figure 5) compared to unsealed (Figure 4) pans, due to the presence of thermal decomposition products in sealed pans.
5. The loss of crystalline structure in sucrose is caused by the onset of thermal decomposition, not **thermodynamic** melting.

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Notes

The authors declare no competing financial interest.

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