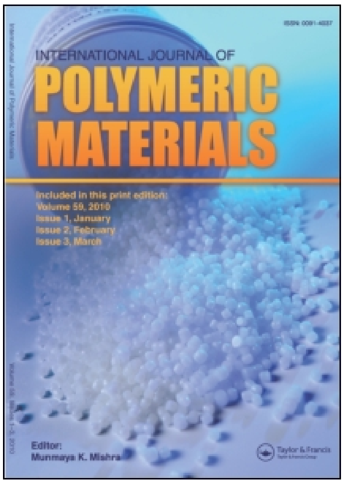

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Abd-Elrahman, M. I. and Ahmed, S. M.(2009) 'Thermal Degradation Kinetics and Geometrical Stability of D-Sucrose', International Journal of Polymeric Materials, 58: 6, 322 — 335

To link to this Article: DOI: 10.1080/00914030902859273

URL: http://dx.doi.org/10.1080/00914030902859273

International Journal of Polymeric Materials, 58:322–335, 2009
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ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030902859273

Thermal Degradation Kinetics and Geometrical Stability of D-Sucrose

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Thermal degradation kinetics of solid-state D-sucrose and D-glucose were studied using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) techniques. The melting and decomposition process of the two sugars were displayed as endothermic peaks on the DTA curve under nonisothermal conditions. It was noticed that the melting peak temperature of D-glucose was lower than that of the other sugar. For the decomposition processes, the opposite occurred. The decomposition kinetic parameters, such as the decomposition activation energy (E_d) and the frequency factor (K_o), were calculated by employing different approximations. The relative stability of the studied sugars was determined. Molecular mechanics (MM) calculations showed that the optimal geometric structure (OMG) of D-sucrose was at least three orders of magnitude more stable than the molecular geometric (MG) structure. These calculations indicate that the potential energy (PE (kcal mol^{-1})) of the OMG is about three (1.142×10^3) orders of magnitude lower than the MG structure of the same sugar. So, optimizing the geometry of the molecular structure (OMG) is very important for understanding the stability of this sugar.

Keywords: D-glucose, D-sucrose, DTA, molecular mechanics calculations, TG, thermal degradation

INTRODUCTION

Glucose and sucrose are the most common sweeteners with increasing production worldwide. Caramelization of these compounds takes place during food processing applications. The analyses of sucrose and

Received 7 January 2009; in final form 12 January 2009.

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glucose and other sugars are the most widespread physical and chemical analyses performed within the industries of food, forage, biomass, pulp and paper, among others. Among medical applications of glucose, it was found that incubation of rat tail tendon with glucose showed an increase in collagen crosslinking expressed as an increase in shrinkage temperature [1].

It has been reported that the primary reaction of the thermal degradation of sucrose is the splitting of glycoside bond at 185°C [2]. In a DSC study of sucrose, the appearance of an endotherm at 150°C has been found, as well as the expected main melting peak of sucrose at 190°C [3]. Some sugars may caramelize and become brown concomitantly with the melting process but they may also decompose before melting [4]. If the enthalpy related to decomposition is smaller than the enthalpy of melting, the total enthalpy is lower if the decomposition begins before melting occurs and the total enthalpy is larger if decomposition happens after the melting peak.

Deferential thermal analysis (DTA) is a useful technique for determining the decomposition temperatures. The shape of the DTA peak depends strongly on the test conditions and parameters. For example, the position of the peak maximum changes with the rate of heating, the thermal conductance and the sample mass. Only the extrapolated onset temperature is relatively independent of experimental parameters. The melting temperatures of sugars are sensitive to water, impurities and crystallinity [4]. As far as we know there is no information available about the determination of the kinetic parameters of thermal degradation of crystalline sucrose and glucose. A survey of the literature reveals that the thermal degradation pattern of sugars has not been seriously dealt with, involving the various kinetic equations and related parameters.

The aim of this study is to find out the decomposition kinetic parameters, such as the activation energy and the frequency factor of the splitting of glycosidic bonds, using the DTA and TGA techniques. The decomposition rates were also calculated to determine the decomposition mechanism of the investigated sugars. We, therefore, heated the samples at temperatures considerably above their melting point.

EXPERIMENTAL

Materials

Granulated analytical grade sucrose from Fisher Chemicals (FC: heavy metals $\leq$ppm Pb; sulfated ash $\leq$0.01% insoluble matter

$\leq 0.05\%$; titratable acid ≤ 0.0008 meqiv/g; invert sugar $\leq 0.05\%$; SO_4, SO_3 as SO_4; $Cl \leq 50$ ppm; $Fe \leq 5$ ppm obtained from Fisher Scientific Catalogue 22004–2005) and high-ash granulated sugars from Silver Spoon (SP). D-glucose was obtained from Fluka Biochemical Co.; the purity is $>99.5\%$. Before measurements all samples were dried at 50°C for two days and then stored in a desiccator over P_2O_5.

Instrumentation

The TG measurements were carried out using the Shimadzu thermal analysis apparatus (DTG-60H). The degradation was studied by using a Sartorius electrobalance (Type 2004 MP6). The sample was placed in a quartz basket suspended from the arm of the balance by means of a quartz wire. The sugars were heated at different heating rates (5–35°C $\min^{-1}$). The sample temperature was adjusted using a Heraeus temperature controller (Type TRK). Glucose and sucrose sugars were identified in the negative-ion mode using a JMS-600 H mass spectrometer (JEOL, Tokyo, Japan) equipped with a FAB ion source and a collision cell. A fast atom helium beam was generated from He^+ ions which were accelerated to 70 V unless otherwise noted.

Method of Calculations of Molecular Mechanics

MM+ calculations including MM2 and MMP2 force field [5] were carried out assuming the investigated molecule in the gas phase. The values of potential and geometrical energies as well as the dipole moment were obtained considering dPE = 0.42 J and the normal method [5]. The search for a minimum energy of the molecule geometry resulted in a 3D structure. MM+ calculations iteratively change the position of atoms towards the structure characterized by lower energy until the molecule internal energy has been minimized.

The energy of a molecule is influenced by the atomic coordinates and could be calculated according to the equation [5]

$$E(x) = E_{str} + E_{ang} + E_{stb} + E_{oop} + E_{tor} + E_{vdw} + E_{ele} + E_{sol} + E_{res} \quad (1)$$

where E_{str} is the bond stretch, E_{ang} is the bond angle bend: E_{stb} is the stretch-bend: E_{oop} is the out-of-plane, E_{tor} is the torsion: E_{vdw} is the van der Waals, E_{ele} electrostatic, E_{sol} is the implicit solvation, and E_{res} restraint energy.

RESULTS AND DISCUSSION

Molecular Mechanics Calculations

A MM treatment of the proposed formula was used to estimate the potential energy (*PE*) in kJ mol^{-1} and dipole moment (μ) of the MG and OMG proposed structure of the sugar under investigation. These calculations (Table 1) indicate that the *PE* and μ of the MG (Scheme 1a) is about three (1.142×10^3) orders of magnitude higher than the OMG (Scheme 1b) structure of the same matrix. So, optimizing the geometry of the molecular structure (OMG) is very important for understanding the stability of this sugar. The negative value of *PE* and μ of this sugar (D-sucrose) indicates that the proposed geometric configuration for this sugar is the most stable.

MS Spectra of Glucose and Sucrose

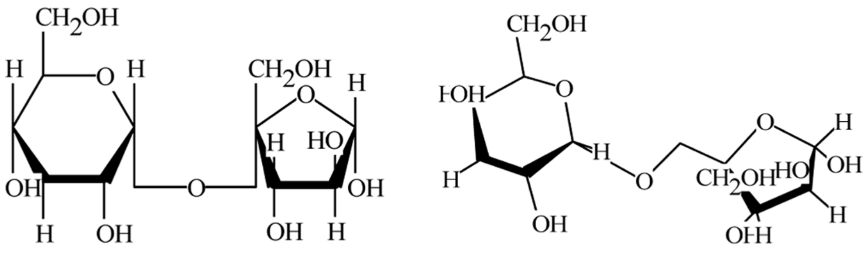
Mass spectrum (MS) is a useful technique for the identification of the sugars under investigation (Figure 1). The peaks appearing at m/z: 44, 55, and 57 are due to the CO_2, C_3H_3O and C_3H_5O molecules. The peak (base peak) at m/z 60 could be assignable to $C_2H_4O_2$. The intense fragment at m/z 73 could be assignable to $C_3H_5O_2$. The peaks appearing at higher mass, m/z 86, 91, 103 and 119, were due to the full-scale sugar degradation, as seen in Figure 1a. Mass spectrum of sucrose shown in Figure 1b gave the same fragments as in D-glucose, especially at higher molecular mass. The intense fragment (base peak) at m/z 73 could be assignable to $C_3H_5O_2$. The peak appearing at m/z 149 could be assignable to $C_6H_{13}O_4$. The other fragments at higher mass, m/z: 221, 274 and 293, could be assignable to the degradation of sugar backbone.

Thermal Gravimetric Analyses of Glucose and D-Sucrose

TG of D-glucose and D-sucrose were carried out at different heating rates as shown in Figure 2, and Tables 2 and 3. Increasing the rates of heating the sugars shows increases of the mass loss in all samples studied. Three steps of mass loss (Tables 2 and 3) were found. The

TABLE 1 MG and OMG Energies (kcal mol^{-1}) and μ (Debye) of Sucrose Sugar

Sugar/Parameter	PE	OMG	μ
Sucrose (MG)	2414.495	—	7.12
Sucrose (OMG)	−2.115	1.77	7.70

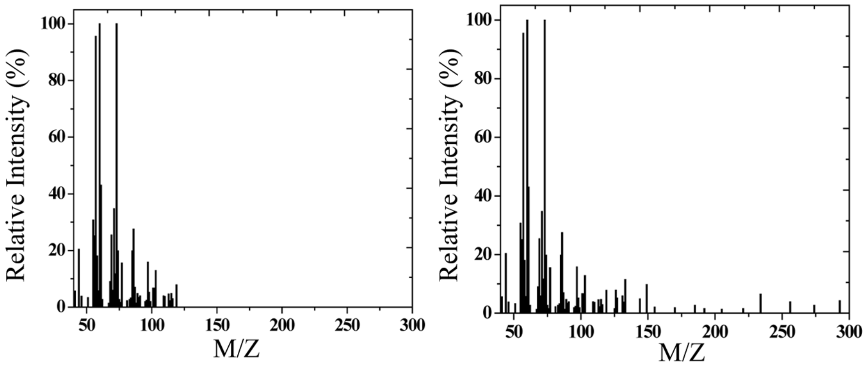


(a) (b)

SCHEME 1 (a) Molecular geometric (MG); and (b) Optimum molecular geometric (OMG) of D-sucrose, using MM calculations.

initial mass loss (2.68–1.63%) between 20 and 100°C could be attributed to the loss of moisture. The proportion of moisture decreases with increasing the heating rate ($r \geq 0.992$). The peak corresponding to this step was found to be shifted to higher temperature (72.7–92.6°C) as seen in Table 2. The mass loss increases linearly ($r \geq 0.993$) with increasing the heating rate. The second step was between 100 and 250°C. This step could be attributed to the melting of the D-glucose sample. The enthalpy of this step was found to increase with increasing the heating rate. The higher weight loss of this step is about 24% at lower heating rate (5°C min^{-1}).

The thermal behavior of D-sucrose did not show the step for moisture. The first step occurring in the range of 20–250°C was due to the melting of this sugar. The peak position was shifted to a higher temperature from 170 to 196 with increasing the heating rate from 5 to 35°C min^{-1}. The



(a) (b)

FIGURE 1 Mass spectra of: (a) D-glucose, (b) and D-sucrose.

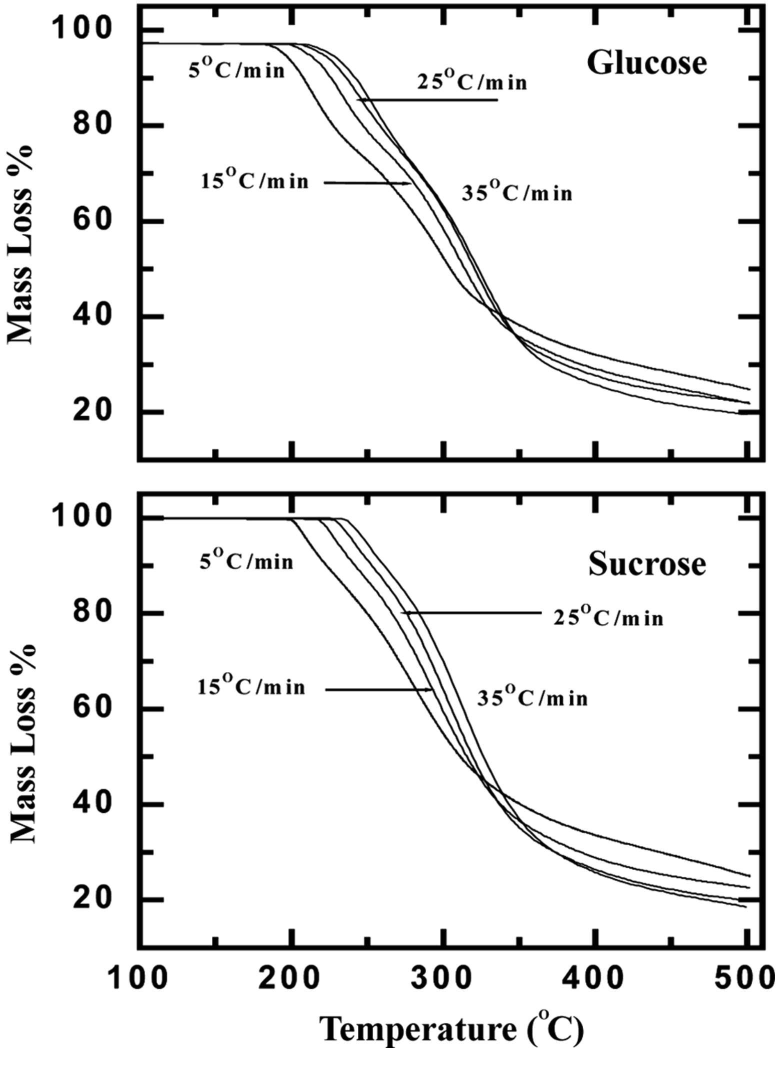


FIGURE 2 TG of D-glucose and D-sucrose at different heating rates.

second step could be assignable to the decompositon of the sugar and was also highly dependent on the heating rate.

Differential Thermal Analysis

The differential thermal analyses (DTA) thermograms of both D-glucose and D-sucrose were taken at different heating rates (α)

TABLE 2 Results of TG and DTA of Glucose

Heating rate/°C min^{-1}	Temp. range	Mass loss, mg/%	Peak/°C	ΔH/Jg^{-1}
5	20–100	0.161 (2.68)	72.7 ± 0.9	175.84
	100–250	1.470 (24.45)	212.4 ± .3	251.27
	251–345	2.036 (33.90)	—	—
	346–500	0.84 (14.01)	—	—
15	20–100	0.135 (2.47)	81.13 ± 0.4	188.64
	100–265	1.456 (23.74)	150.5 ± 0.9	395.41
	266–370	2.442 (40.15)	305.2 ± 0.7	32.65
25	30–100	0.153 (2.09)	86.2 ± 0.2	148.24
	100–204	0.017 (0.23)	156.4 ± 0.5	363.23
	205–284	1.63 (27.16)	246.7 ± 0.8	305.66
35	25–100	0.074 (1.71)	92.6 ± 0.6	12833
	101–287	1.738 (28.85)	163.1 ± 0.9	313.16
	288–500	2.957 (48.90)	313.2 ± 0.1	26.62

at 5, 15, 25 and 35°C min^{-1} under nonisothermal conditions. In DTA measurements, we are concerned with the decomposition process of both sugars.

The results of DTA measurements are presented in Figures 3 and 4. Each DTA curve illustrated two peak temperatures for the melting and decomposition processes. In addition, lower peak temperatures in D-glucose curves attributed to the loss of moisture are also shown. The peaks of D-sucrose and D-glucose were almost normal melting and decomposition peaks [2–4]. Increasing the rates of heating (α) moves the onset and the peak temperatures of decomposition (T_d) to higher temperatures. For D-glucose, as shown in Figure 3, when α changes

TABLE 3 Results of TG and DTA of D-Sucrose

Heating rate/°C min^{-1}	Temp. range	Mass loss, mg/%	Peak/°C	ΔH/Jg^{-1}
5	18–236	0.882 (14.49)	170.1 ± 0.4	461.73
	237–352	2.818 (46.31)	206.7 ± 0.2	188.24
15	30–212	0.011 (0.18)	187.6 ± 0.2	482.37
	213–251	0.81 (13.27)	232.3 ± 03	216.08
	252–500	3.21 (63.40)	—	—
25	22–266	0.794 (13.17)	191.2 ± 0.6	396.12
	262–374	3.405 (56.42)	247.4 ± 0.9	153.18
	375–500	0.598 (9.92)	315.7 ± 0.2	50.93
35	20–266	0.728 (11.95)	196.1 ± 0.3	143.78
	267–400	3.776 (61.99)	253.9 ± 0.4	120.67
	400–500	2.430 (7.13)	321.6 ± 0.8	67.25

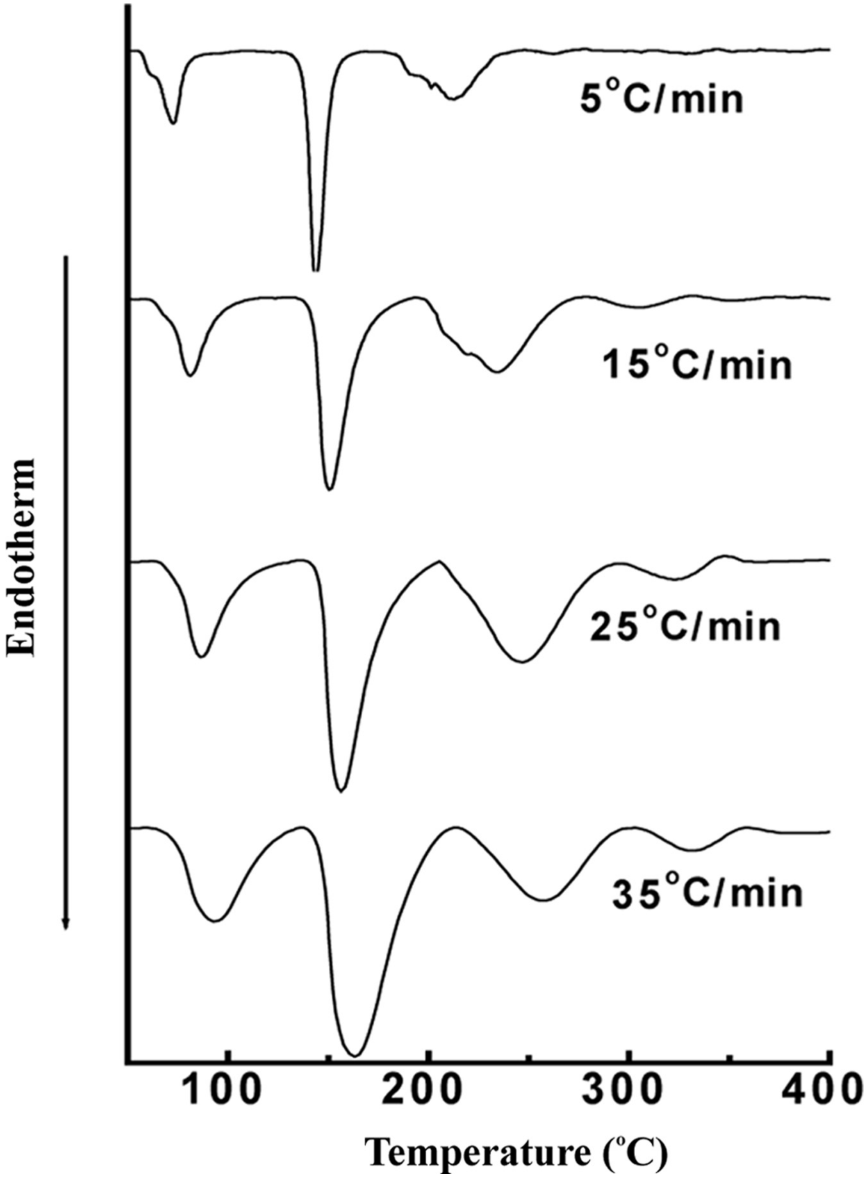


FIGURE 3 DTA curves of D-glucose at different heating rates.

from 5 to 35 min^{-1}, the melting peak temperature (T_m) moves from 146 to 160°C and the decomposition peak temperature T_d from 212 to 265°C. As shown in Figure 4, for the same α changes, T_m for D-sucrose

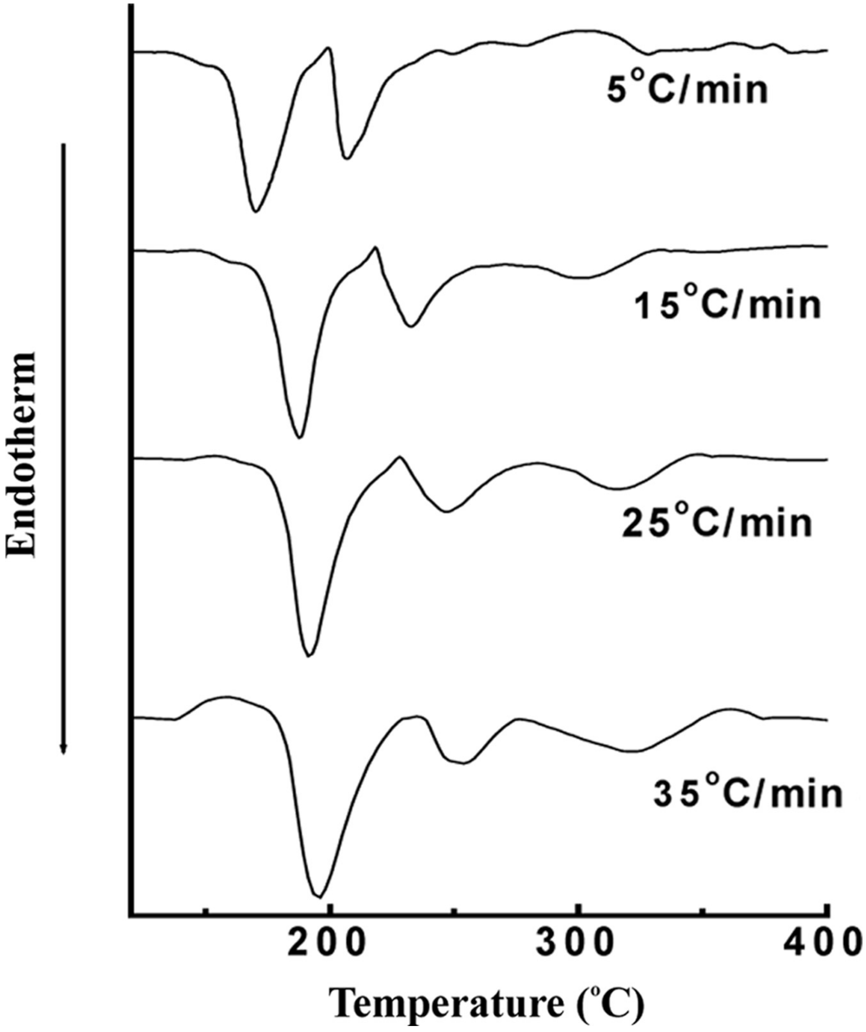


FIGURE 4 DTA curves of D-sucrose at different heating rates.

moves from 170 to 196°C and T_d from 207 to 245°C. The changes in T_m with the heating rate for both sugars indicate that D-sucrose is more thermally stable than D-glucose. Also, the latter melts in a temperature interval narrower than that of D-sucrose. From the changes of T_d for both sugars, the D-sucrose sugar thermally decomposes prior to D-glucose sample since the decomposition peak temperature of D-sucrose was lower than that of the other sugar. At slow rates of heating, the decomposition peak of D-glucose is not sharp but wide and has a saw-tooth appearance; the start of decomposition is also seen. The results of the DTA thermal behavior of these sugars are supported by the present TGA study.

The decomposition kinetic parameters of the glucose and sucrose chains were investigated using DTA and TG techniques. In order to analyze the kinetic parameters of decomposition, the Kissinger and Augis & Bennet plots approaches [6,7], proposed for usual chemical reactions, has been applied using nonisothermal techniques. From this, the kinetic parameters of decomposition can be calculated from a set of DTA curves. The decomposition peak temperature (T_d) relates to the rate of heating (α) by the following equations [6,7]:

$$\ln\left(\frac{\alpha}{T_d}\right) = -\left(\frac{E_d}{R}\right)\frac{1}{T_d} + K_0 \tag{2}$$

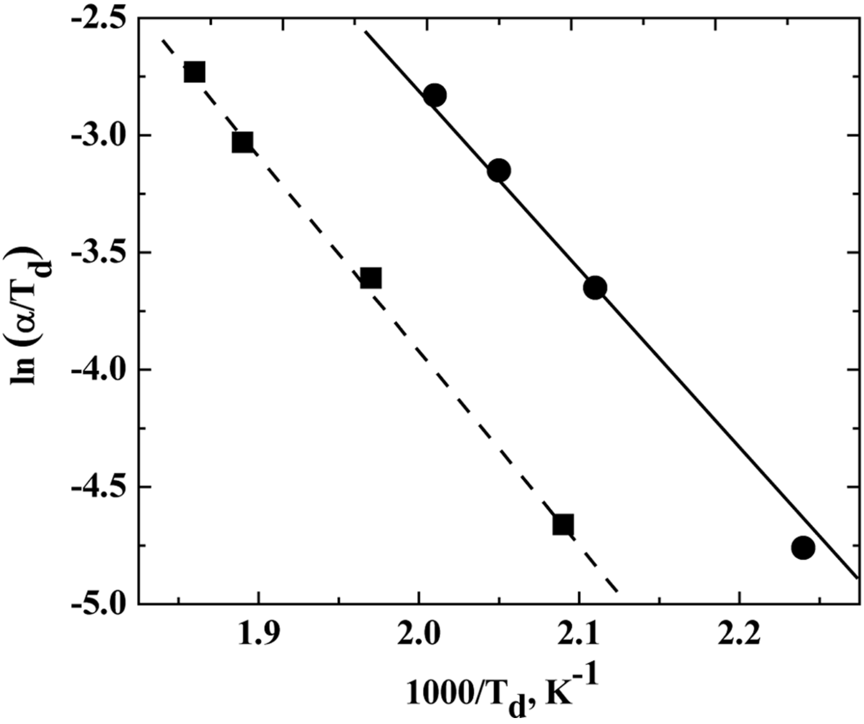


FIGURE 5 Plot of ln(α/T_d) *vs.* (1/T_d) of D-sucrose (circles, solid line) and D-glucose (squares, dashed line).

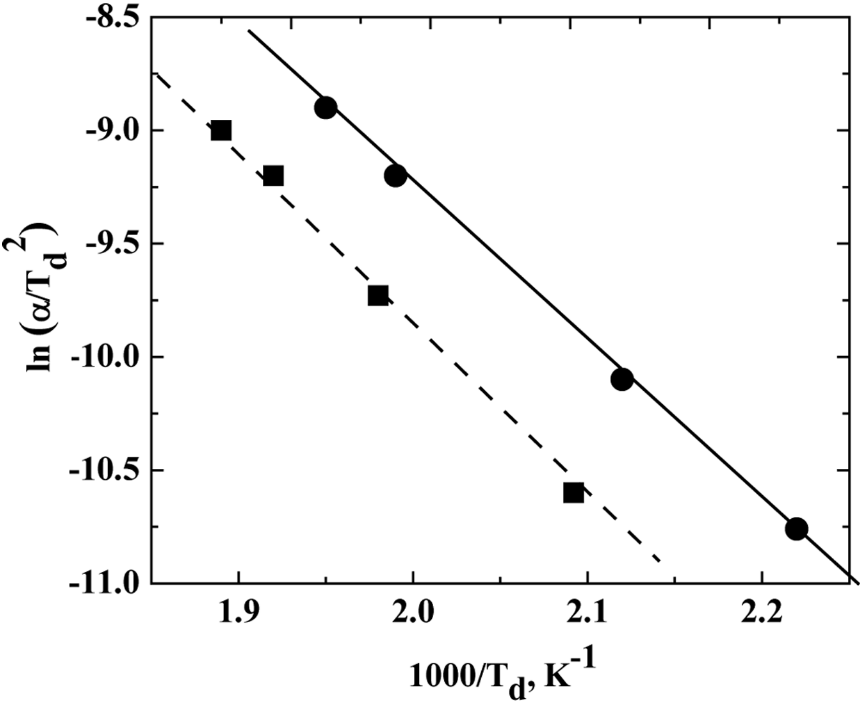


FIGURE 6 Plot of ln(α/T_d^2) *vs.* ($1/T_d$) of D-sucrose (circles, solid line) and D-glucose (squares, dashed line).

$$\ln\left(\frac{\alpha}{T_d^2}\right) = -\left(\frac{E_d}{R}\right)\frac{1}{T_d} + const. \tag{3}$$

where R, E_d and K_o are the gas constant, activation energy and frequency factor, respectively.

We have effectively applied these approaches to determine the kinetics of solid-state stability of glycine as a model for peptides [8]. Based on Eq. (2), plotting ln(α/T_d) vs. ($1/T_d$) gives a linear relation. The experimental points show a good fit with Eq. (3), as shown in Figure 5. The experimental data of glucose and sucrose, shown in Figures 5 and 6, were multiplied by a factor to avoid the overlaps. The values of E_d were calculated from the slopes of the original fitted straight lines to the experimental data, and the values of K_o were also estimated from the original intercept of the lines with vertical axes. The application of Eq. (2) yielded E_d to be 88.86 ± 3.2 and $81.48 \pm 2.4\,\text{kJ mol}^{-1}$ for glucose and sucrose, respectively. Although the melting process of glucose begins at $T = 146°\text{C}$ (for

$\alpha = 5°C\,min^{-1}$) before that of sucrose ($T = 170°C$), the thermal decomposition of glucose was slightly more stable than the latter, having a little lower E_d. The small deference in the values of E_d of both reflects the slight deference in the peak temperatures of the decomposition process, as seen from Figures 3 and 4.

Figure 6 shows a good fit between the experimental points and the straight lines according to Eq. (3). E_d of both is estimated to be 84.63 ± 3.3 and $77.31 \pm 2.5\,kJ\,mol^{-1}$ for glucose and sucrose, respectively.

The frequency factor K_o, as decomposition parameter, measures the probability of molecular decomposition. It was calculated from the intercept of the straight fitting lines with vertical axis (Eq. (2)) and was found to be 39.7×10^6 and $7.70 \times 10^6\,min^{-1}$, respectively, for D-glucose and D-sucrose samples. Although glucose has higher decomposition activation energy than that of sucrose the frequency factor of glucose is five times greater than that of the other. This

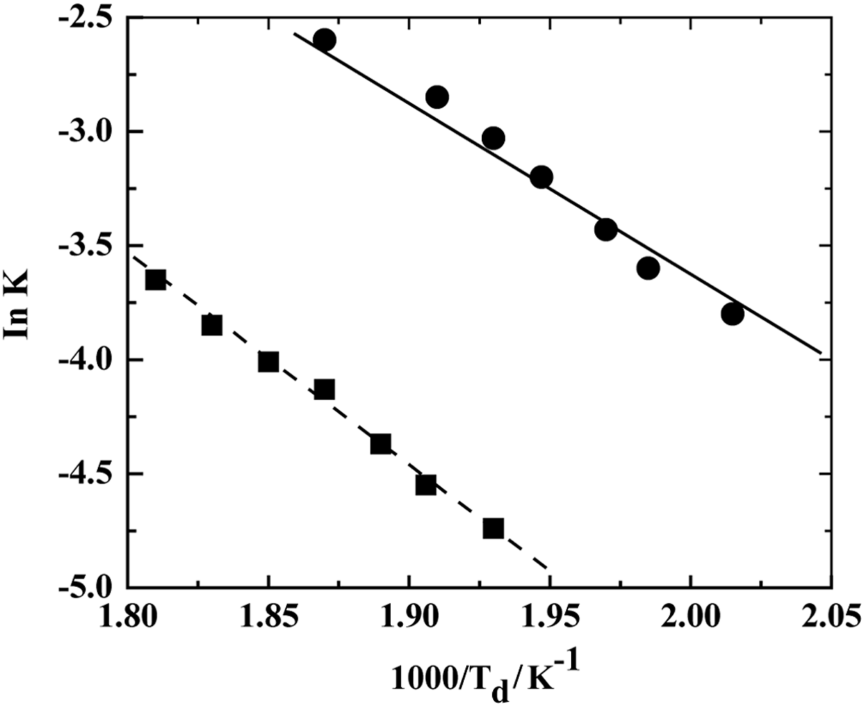


FIGURE 7 Temperature dependence of the decomposition rate constant for D-sucrose (circles, solid line) and D-glucose (squares, dashed line). at constant heating ($25°C\,min^{-1}$) rate.

means that, according to the definition of the K_o, glucose decomposed quicker than sucrose while the latter started the decomposition process before the D-glucose.

The decomposition rate constant (K), defined as the effective overall decomposition rate at any temperature T in the entire region of endothermic peak, is usually assumed to have an Arrhenian temperature dependence.

$$K = K_0 \exp(-E_d/RT) \tag{4}$$

Substituting the obtained values of E_d and K_o from Eq. (2), one can calculate K as a function of T for each heating rate. The calculated values of $K(T)$ for glucose and sucrose samples at a constant heating rate were plotted as $\ln K$ vs. $1/T$ and the straight lines are shown in Figure 7. The validity of Eq. (4) for each heating rate confirms that the results obtained for E_d and K_o. From Figure 7, it can be noticed that the sucrose sugar thermally decomposes prior to glucose. This result is confirmed by the obtained values of E_d which relates to the stability for these sugars as calculated from Eqs. (2) and (3).

CONCLUSIONS

Kinetic parameters of the thermal decomposition of D-glucose and D-sucrose were studied using differential thermal analysis (DTA) and thermogravimetric analysis (TG) techniques. The melting and decomposition process of D-glucose and D-sucrose were displayed as endothermic peaks on the DTA curve. The kinetic parameters, such as the decomposition activation energy (E_d) and the frequency factor (K_o), were calculated by employing different approximations. The relative stability of the studied sugars was determined. It was found that the D-glucose decomposes later and quicker than the D-sucrose sample. Molecular mechanics (MM) calculations suggest that the optimal geometric structure (OMG) of D-sucrose is at least three orders (1.142×10^3) of magnitude more stable than the molecular geometric (MG) structure.

REFERENCES

[1] Mentink, C. J. A. L., Hendriks, M., Levels, A. A. G., and Wolffenbuttel, B. H. R., *Clinica Chimica Acta* **321**, 69 (2002).
[2] Simkovic, I., Surina, I., and Vrican, M., *J. Anal. Appl. Pyrolysis* **70**, 493 (2003).
[3] Beckett, S. T., Francesconi, M. G., Geary, P. M., Mackenziea, G., and Maulnya, A. P. E., *Carbohydr. Res.* **341**, 2591 (2006).

[4] Roos, Y. (1995). *Phase Transitions in Foods*, Academic, San Diego.

[5] Burkert, U., and Allinger, N. L. *Molecular Mechanics*, ACS Monograph 177, American Chemical Society: Washington, DC, 1982.

[6] Kissinger, H. E., *Anal. Chem.* **29**, 1702 (1957).

[7] Augis, J. A., and Bennett, J. E., *J. Electrochem. Soc.* **125**, 330 (1978).

[8] Abd-Elrahman, M. I., Ahmed, M. O., Ahmed, S. M., Aboul-Fadl, T., and El- Shorbagi, A., *Biophys. Chem.* **97**, 113 (2002).