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KINETIC STUDIES ON THE THERMAL DECOMPOSITION OF GLUCOSE AND FRUCTOSE

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The thermal decompositions of glucose and fructose were studied by means of the Derivatograph. From the melting temperature up to 300° these monosaccharides decompose and give brown caramel matter. The TG curves as functions of time were taken at various heating rates (0.5 – 10°/min) by the Derivatograph and the activation energies of the decompositions were determined by Ozawa's method.

The browning of food products and their raw materials on heat-treatment during storage and processing is associated in most cases with the alterations of carbohydrates. Since the brown colouration is indicative of a decrease in nutrient and biological value, and leads in only a few cases to advantageous changes, the planning of the processes and their influencing in a favourable direction from a knowledge of the mechanism and kinetics is of great importance.

Caramel formation was selected as model system for the investigations, since in the relatively simple model system identical decomposition products can be observed as in the case of Maillard's reaction observed in food products, and they presumably lead to colour formation through the same route [1].

Caramelization, one of the difficult problems in the thermal treatment of sugars, was achieved with a MOM Paulik – Paulik – Erdey Derivatograph, permitting a reproducible and well-defined heat-treatment.

The individual decomposition stages can be well distinguished in the thermal curves, recorded with linearly increasing temperature, and changes proceeding in the "heating" section can also be taken into consideration. The separation of overlapping processes is made possible by the DTG curve.

The behaviours of several carbohydrates have been studied earlier with the Derivatograph, but the information given by the derivative curves has not been compared with the results of the chemical analysis of the residue and the volatile products, so that conclusions drawn from the curve are not always well established [2].

In earlier investigations [3], glucose and fructose samples were mixed with aluminium oxide and heat-treated; after cooling at different stages of the decomposition and dissolution in water, the quantities of residue, colouring substances and other components were determined by chemical analysis. In addition, an identical sample was heat-treated in a closed system having the same temperature program as the previous one, and the volatile decomposition products were also determined. As a result of these investigations, the glucose and fructose thermal curves shown in Figs 1 and 2 can be interpreted as follows.

Fig. 1 shows the thermal curves of glucose recorded at a heating rate of 6°/min. The minimum at 165° on the DTA curve indicates the endothermic effect of the melting of the sugar. The TG curve shows that the weight of the sugar does not change up to the melting point. With the melting of glucose its decomposition begins, and three reaction stages can be distinguished.

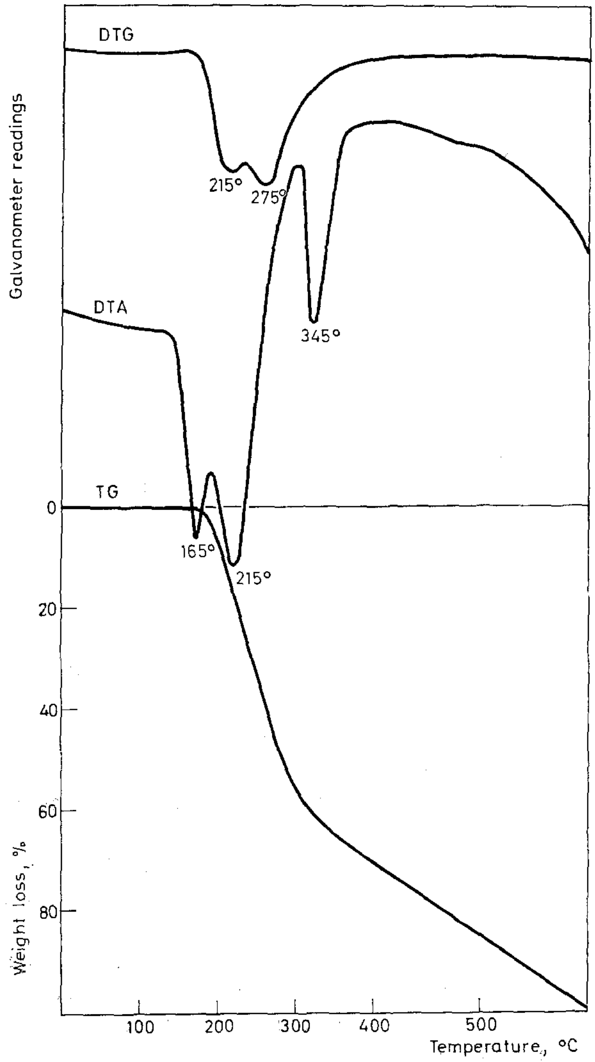

Fig. 1. Thermal curves of glucose (500 mg glucose + 1 g Al_2O_3)

The first decomposition stage begins on melting, and terminates at 240°. This stage is accompanied by about the same endothermic effect as the heat of melting, and the course of the reactions in this stage is not affected by air. The 25% loss in weight is the result of two main processes. Part of the glucose polymerizes with the formation of oligo- and polysaccharides. This process is accompanied by the formation of water, which evaporates at these temperatures.

The residual glucose decomposes with the formation of oxo and other unidentified compounds, including brownish colouring matter. At 240°, no glucose or oligo-

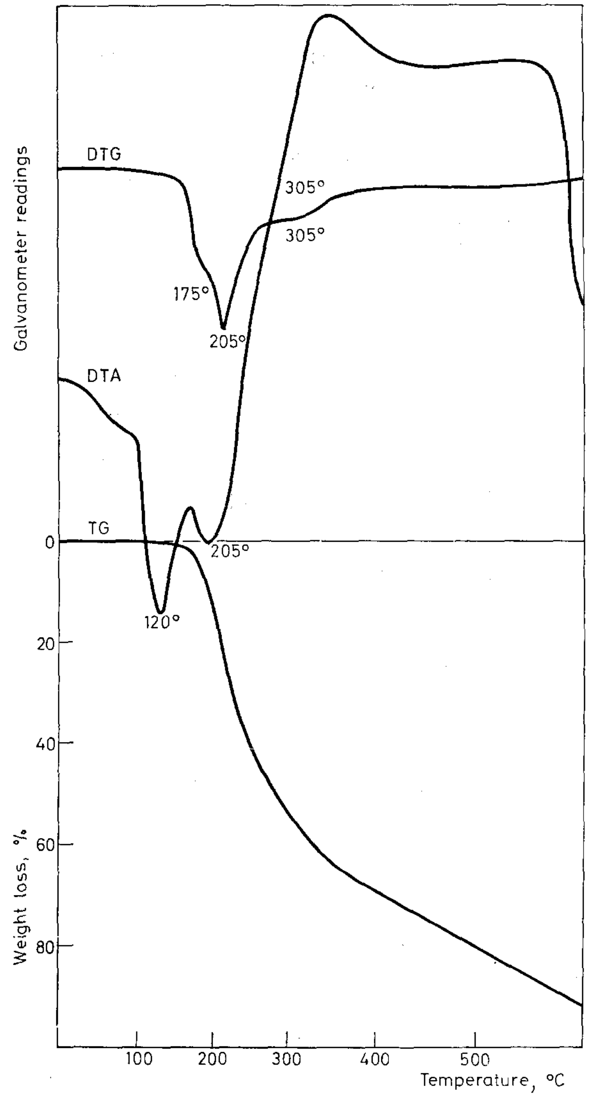

Fig. 2. Thermal curves of fructose (500 mg fructose + 1 g Al_2O_3)

saccharides can be detected, these presumably having been decomposed and converted to brown colouring matter.

In the next decomposition stage, the brown colouring matter and the accompanying polysaccharide are decomposed, the former becoming insoluble and the polysaccharide also being converted to insoluble brown matter. The decomposition products formed, consisting of the most diverse substances, are ignited in air.

Figure 2 shows the thermal curves of fructose, recorded under the same conditions as those of glucose. In the case of fructose, identical stages can be observed, but fructose melts at 120°, while the DTG curve shows the decomposition to proceed in two steps up to 240°. The first step, up to 180°, is slower, with 10% loss in weight. Mainly oligosaccharides of diketerolevulosane type are formed in this stage. In the second step, from 180 to 240°, these are decomposed together with the residual fructose into brown colouring matter, while several oxo and other compounds can be detected in the volatile fraction.

As no polysaccharide is formed in the case of fructose in the stage between 240 and 400°, less decomposition products are formed, but as in the case of glucose the total loss in weight is 69%.

The final decomposition stage of fructose is completely identical with that of glucose.

Ozawa's [4] method was used to elucidate the kinetics in the most important first stage of the decomposition up to 240°, since the curves do not represent the changes under isothermal conditions. Using the approximation of Doyle, Ozawa derived the following relationship:

$$\log a = \log \left(\frac{Z}{-\int\limits_{W_0}^{W} \frac{\mathrm{d}W}{W^2}} \cdot \frac{\Delta H}{R} \cdot 4.482 \cdot 10^{-3} \right) - 0.4567 \frac{\Delta H}{RT}$$

where:

a = heating rate (°C/min)
Z = pre-exponential factor
n = order of reaction
H = activation enthalpy (cal/mole)
W, W_0 = weights of the sample in mg
R = gas constant (cal/mole °K)
T = absolute temperature (°K)

Thus, there is a linear relationship between the logarithm of the heating rate and the reciprocal of the temperature for identical losses in weight on TG curves recorded at various heating rates. The activation energy of the reaction can be calculated from the slope of the line.

The thermal curves were recorded on identically prepared samples at various heating rates (0.5 – 8.0 °C/min), and from these the loss in weight vs. $\frac{1}{T}$ curves

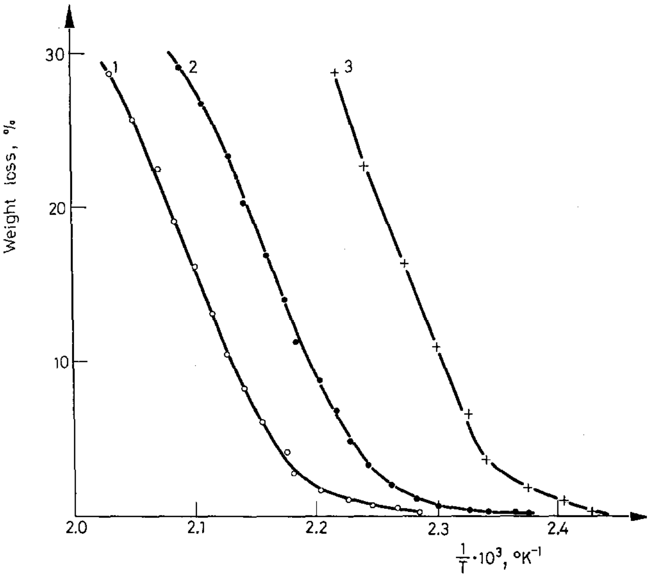

Fig. 3. Weight loss vs. $\frac{1}{T}$ diagram at different heating rates (500 mg glucose + 1 g Al_2O_3).
1. 7.4 °C/min; 2. 2.7 °C/min; 3. 1.1 °C/min

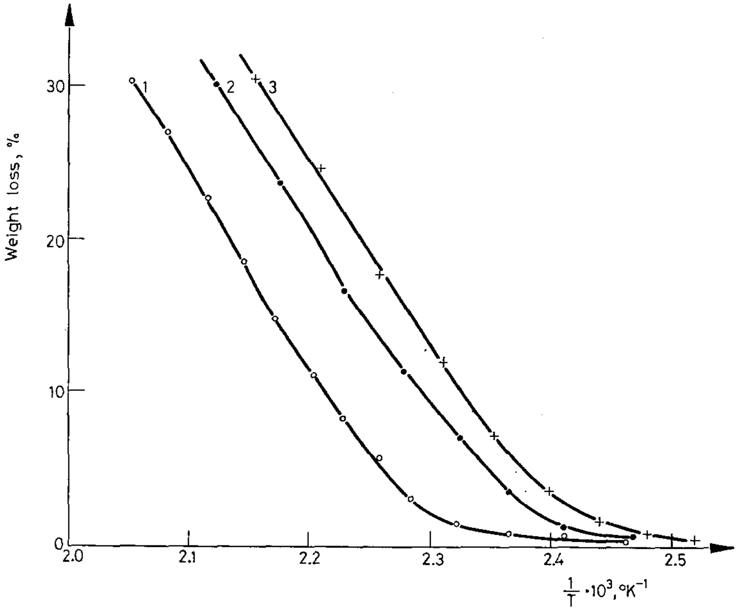

Fig. 4. Weight loss vs. $\frac{1}{T}$ diagram at different heating rates (500 mg fructose + 1 g Al_2O_3).
1. 7.0 °C/min; 2. 2.1 °C/min; 3. 0.92 °C/min

were plotted; three curves for glucose and three for fructose are shown in Figs 3 and 4. From these curves, the temperatures relating to identical losses in weight were read off, and the log *a* values plotted versus $\frac{1}{T}$. The equation of the line was determined by the least squares method, and the activation energy was calculated from the slope. Readings and calculations were made up to 30% loss in weight within the range investigated, and the activation enthalpy was plotted as a function of the loss in weight (Fig. 5).

Completely identical curves were obtained for glucose and fructose, the derivations not exceeding the value of the random error, ±3 kcal/mole.

For both sugars the activation energy decreases from the initial value of 26 kcal/mole to 18 kcal/mole, and then increases again to an average value of 26 kcal/mole.

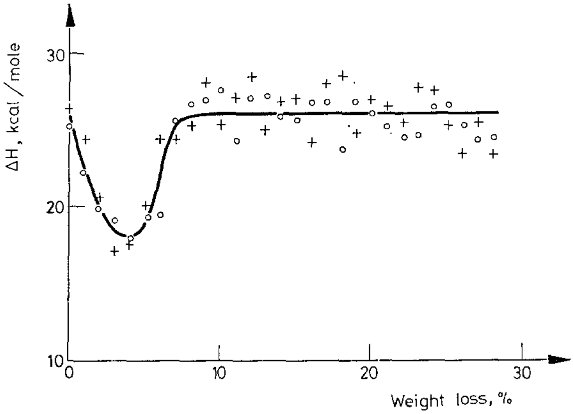

Fig. 5. Activation energy vs. weight loss diagram, for fructose +, glucose ○

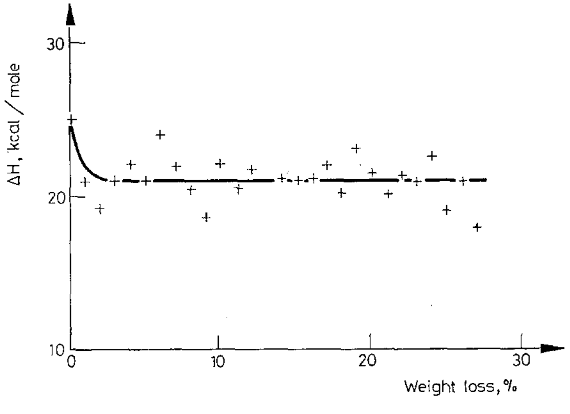

Fig. 6. Activation energy vs. weight loss diagram for a mixture of 100 mg glucose + 20 mg Na_2CO_3 + 1 g Al_2O_3

This value is in good agreement with the 28 kcal/mole activation energy of glucose degradation obtained under isothermal conditions, and also with the value of 30 kcal/mole determined for 5-hydroxymethylfurfurol formation for both sugars.

The minimum observed in the activation energy at the beginning of the decomposition can be ascribed to the alkali metal ions extracted from the aluminium oxide by the sugar. When anhydrous sodium carbonate equivalent to ten times the sodium extractable from the aluminium oxide was added to the mixture, the activation energy vs. loss in weight curve was modified as shown in Fig. 6.

The activation energy is decreased by this great quantity of sodium ions to 21 kcal/mole. When pure aluminium oxide is used the curve returns to the initial value of 26 kcal/mole, because the acids formed neutralize the alkali metal ions, this being impossible in the case of a tenfold quantity.

Thus, the method gives values for the activation energy which agree well with those obtained in isothermal investigations. The activation energy is suitable for the characterization of the catalytic effect of additives (in the present case sodium ions) which influence the reaction.

References

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Résumé — On a étudié la décomposition thermique du glucose et du fructose à l'aide du "Derivatograph". Ces monosaccharides subissent une décomposition à partir de la température de fusion jusqu'à 300 °C en donnant des caramels bruns. Les courbes TG ont été enregistrées en fonction du temps avec diverses vitesses de chauffage (de 0.5 °C/min jusqu'à 10 °C/min) et l'énergie d'activation de la décomposition a été déterminée par la méthode d'Ozawa.

Zusammenfassung — Die thermische Zersetzung von Glukose und Fruktose wurde mit Hilfe des Derivatographen studiert. Diese Monosaccharide erleiden von der Schmelztemperatur bis zu 300 °C eine Zersetzung und ergeben braune Karamelstoffe. Die verschiedenen Zeitspannen zugeordneten TG-Kurven wurden vom Derivatographen bei verschiedenen Aufheizgeschwindigkeiten (von 0.5 °C/min bis zu 10 °C/min) registriert und die Aktivierungsenergie der Zersetzung wurde mittels der Methode von Ozawa bestimmt.

Резюме — С помощью дериватографа исследован термораспад глюкозы и фруктозы. Начиная с температуры плавления и до 300°С проходит разложение этих моносахаридов и образуется коричневое карамелоподобное вещество. Снята кривая ТГ в зависимости от времени при различных скоростях нагревания (от 0,5°С/мин до 10°С/мин) и определена энергия активации распада методом Озава.