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DTG AND DTA STUDIES ON TYPICAL SUGARS

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ABSTRACT

The DTG and DSC-DTA techniques have been found to be suitable for the investigation of typical sugars between 25ºC and 700ºC. Endothermic and exothermic reaction temperatures and enthalpies of 24 sugars are listed. These data serve not merely to characterize or identify substances, but to yield important information pertaining to the relation between molecular structure and thermal behaviour.

INTRODUCTION

The present study is a systematic investigation into the thermal behaviour of a range of 24 sugars and polysaccharides. DTG and DTA-DSC techniques were used in order to obtain data concerning the changes produced by carbohydrates during their heating. This·information is important for safely directing high temperature processing operations and understanding deterioration phenomena in foods and woods (1)

EXPERIMENTAL

All the samples were supplied by Merck and Sigma. Thermal analysis was performed using a Perkin Elmer 3600 and DTA 1700, as previously reported (2).

RESULTS

The features of tne calorimetric curves were different depending on the type of carbohydrates analyzed. Whereas the polysaccharides mainly exhibit exothermic effects in DTA and only one significative peak in DTG, the shape of these calorimetric curves in the more simple sugars is comparatively rich (Fig.1). Thus, in the mono- and polysaccharides DTA curves, the decomposition exotherms above 300ºC were preceeded by at least two endotherms, one corresponding to the loss of water/fusion (effect 0) and other to an early decomposition (effect I).

The DTA effect II is a slightly endothermic or inflexion that appears just before combustion.

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Relative to their DTG curves, three decomposition steps at 220±40ºC, 310±20ºC and 520±20ºC can be recognized.

It is worth noting, that the first DTG decomposition peak is a polymerization marker while the second DTG effect could be considered as a "fingerprint"-property for each particular sugar with usefulness for characterization purposes.

When through glycosidic linkages the polymerization takes place, the DTG-I peak is shifted to higher temperatures, allowing differentiation among the three groups of the family of carbohydrates. As seen from the data in Table 1, the 180-227ºC DTG peak is characteristic of the decomposition of monosaccharides, while di- and oligosaccharides are decomposed between 236 and 262ºC. In Dextrin, Starch and Cellulose the main process appears above 280ºC.

If the thermoanalytical data of DTG first effects in Table 1 are evaluated from the point of view described previously (see above), it can be concluded that the species differences of the monosaccharides are also reflected in the thermal behaviour of disaccharides or polymeric carbohydrates. For example, if Glucose has a higher thermal stability than Galactose, the disaccharides Cellobiose, Maltose and Trehalose must be more stable than Lactose or Melibiose, such as the facts show.

In like manner, the higher thermal stability of Galactose over Fructose resulted in a higher thermostability of Lactose over Sucrose. So, from DTG-I data, a thermostability sequence can be established for disaccharides:

Cellobiose > Trehalose > Lactose or Maltose > Melibiose > Sucrose

The lower stability of the Fructose moiety (20-40ºC below all the other monosaccharides) is responsible for the irregular low peak DTG-I temperatures for Raffinose and Melezitose vs. disaccharides. For the same reason, Inulin and Ficoll decomposed earlier than other polysaccharides.

Other conclusions also derived from the comparative analysis of the data in Table 1 is that DTG-I and DTG-II maxima are a more suitable tool than the melting points in the characterization of sugars, above all (i) when the melting points of certain carbohydrates are closely near, or (ii) when it deals with hydrated compounds.

Also in basis of DTG effects some other relations could be demonstrated between molecular structure and thermal stability, as follows:

(a) Aldoses are more stable than Ketoses (Fig. 2).

(b) the β-glycosidic linkages confer more thermostability than the α-glycosidic linkages (Fig. 3).

(c) the β-1-4 linkages are more stable than α-1-6, the α-1-1 and α-1-4 being in between...

In the last part of this communication the thermal behaviour above 300ºC of the same range of sugars and polysaccharides early reported is also presented.

TABLE 1

Decomposition endothermal effects of typical sugars (in static air, rate 10ºC/min)

Carbohydrates		effect 0	Onset	effect I		effect II	
		DTA (ΔH)	TG	DTA (ΔH)	DTG-I	DTA	DTG-II
		ºC (cal/g)	ºC	ºC (cal/g)	ºC	ºC	ºC
Monosaccharides							
$C_5H_{10}O_5$	D-Ribose	90 (27)	150	189 (20)	213	279	291
pentoses	D-Xylose	160 (40)	160	198 (11)	203	273	302
	D-Arabinose	167 (46)	173	203 (2)	203	275	313
	L-Arabinose	164 (43)	155	195 (10)	211	263	287
$C_6H_{12}O_6$	D-Mannose	135 (34)	175	205 (58)	222	275	275
hexoses	D-Glucose	156 (33)	192	208 (36)	227	285	321
	D-Galactose	152sh 168 (39)	189	200 (20)	220	285	308
	L-Rhamnose .H_2O	102 (49) 137 (5)	70 150	196 (31)	205	306	299
hexuloses	D-Fructose	121 (39)	149	189 (53)	180	282	267
	L-Sorbose	173 (30)	170	192 (.2)	198	282	266 283
Disaccharides and Oligosaccharides							
$C_{12}H_{22}O_{11}$	D-Trehalose .$2H_2O$	107 119 (56)	94 237	214 (26)	260	297	312 317
	D-Maltose .H_2O	121 (31) 155 (1)	105 205	220 (27)	252	281	315
	Sucrose	180 (27)	215	226 (25)	238	294	294
	D-Lactose .H_2O	150 (35)	126 228	220 230 (68)	246	285	312
	D-Melibiose .H_2O	119 (4) 188 (18)	85 212	223 (15)	239	305	310
	D-Cellobiose	-	236	251 (94)	245sh 262	306	317
$C_{18}H_{32}O_{16}$	D-Raffinose .$5H_2O$	91 (32) 126 (19)	52 213	233 (23)	236	316	301
	D-Melezitose .$2H_2O$	152 (34)	112 216	245 (29)	244	283	287
Polysaccharides							
Homopolysaccharides							
	Inulin	164 (2)	226	233 (13)	242	337	278

TABLE 1 (cont.)

Carbohydrates	effect 0	onset	effect I			
	DTA (ΔH)	TG	DTA (ΔH)	DTG I	DTA	DTG II
	ºC (cal/g)	ºC	ºC (cal/g)	ºC	ºC	ºC
Dextrin	-	230	231 (7) 258 (5)	257sh 287	308	(345)
Starch sol.	-	273	273 (26)	280sh 310	330	-
Cellulose	-	280	-	338	310	-
Heteropolysaccharides						
Ficoll (a syntetic polymer of sucrose)	-	220	-	260sh	300	320 350sh
Hyaluronic acid (sodic salt)	-	220	263 300 (-437)	244-254 290sh	-	398

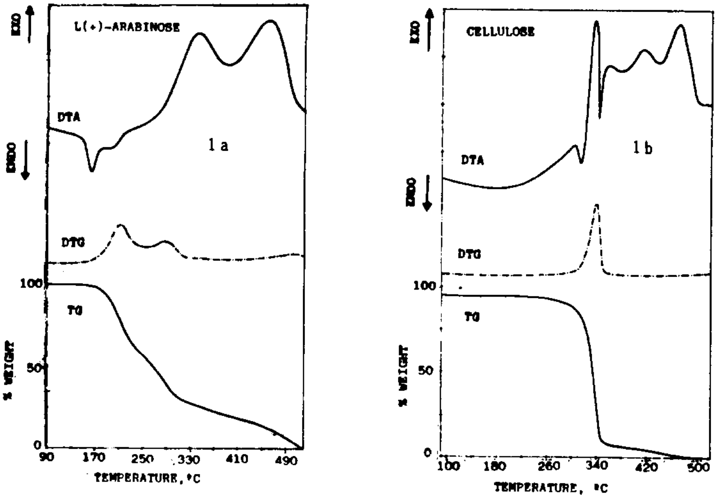


Fig. 1: DTA, DTG and TG thermograms for Arabinose (1.a) and Cellulose (1.b)

Table 2 summarizes the temperatures of the exothermic peaks due to pyrolysis and the respective enthalpies together with the associated DTG effects. These phenomena are related to the samples vaporization and elimination of the volatiles from the reaction zone.

We have found that the observed DTA peaks at 330-410ºC and 440-540ºC for each carbohydrate in particular can be a suitable aid (together with the former effects) for their characterization.

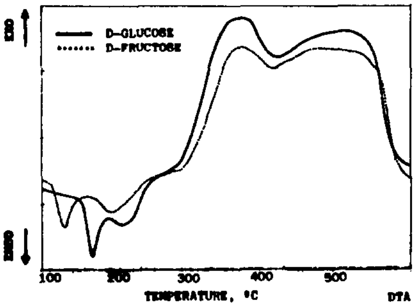
TABLE 2

Decomposition exothermal effects of typical sugars (in static air and at rate of 10ºC/min).

Carbohydrates		effect III	effect IV	effect	combustion	
		DTA	DTA	DTG-III	ΔH	(ΔT)
		ºC	ºC	ºC	cal/g	ºC
Monosaccharides						
$C_5H_{10}O_5$	D-Ribose	335	414 481	536	-1300	(279-506)
pentoses	D-Xylose	332	445	532	-1050	(273-515)
	D-Arabinose	353	454	528	-1318	(275-535)
	L-Arabinose	345	461	503	-1412	(263-550)
$C_6H_{12}O_6$	D-Mannose	357	476	525	-1476	(272-520)
	D-Glucose	373	510	530	-1470	(285-586)
hexoses	D-Galactose	365	471	529	-1616	(285-575)
	L-Rhamnose	357 388	472	510	- 810 -1011	(306-570) (270-570)
	D-Fructose	372	487	537	-1489	(282-599)
	L-Sorbose	367	480	545	-1530	(282-582)
Disaccharides and Oligosaccharides						
$C_{12}H_{22}O_{11}$	D-Trehalose $.2H_2O$	360 395	495	520	-1484	(297-599)
	D-Maltose $.H_2O$	412	492	526	-1575	(280-590)
	Sucrose	379	520	544	-1355	(285-665)
	D-Lactose $.H_2O$	338 413	496	530	-1525	(285-590)
	D-Melibiose $.H_2O$	382	510	523	-1625	(305-600)
	D-Cellobiose	374 488	496	536	-1380	(306-590)
$C_{18}H_{32}O_{16}$	D-Raffinose $.5H_2O$	360 420	503	520	-1255	(280-550)
	D-Melezitose $.2H_2O$	358	484	520	-1422	(285-530)
Polysaccharides						
Homopolysaccharides						
	Inulin	420	565	520	- 928 -1623	(340-596) (235-600)

TABLE 2

Carbohydrates	effect III	effect IV	effect	combustion	
	DTA	DTA	DTG III	ΔH	(ΔT)
	ºC	ºC	ºC	cal/g	ºC
Dextrin	360	516 535	482	- 705 -1130	(308-635) (260-635)
Starch sol.	417 490	594	520	- 614 -1050	(330-630) (273-630)
Cellulose	352 423	480	-	- 912 - 991	(305-520) (220-520)
Heteropolysaccharides					
Ficoll	375	525	522	- 820 -1315	(330-590) (200-590)
Hyaluronic (sodic salt)	413	-	-	- 768	(350-470)



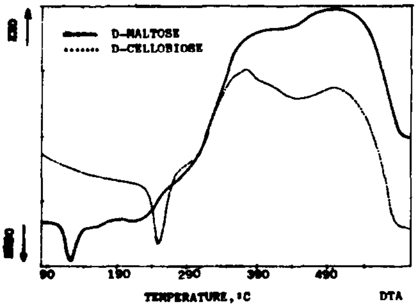


Fig. 2 Thermogram for Glucose and Fructose. Fig. 3 Thermogram for Maltose and Cellobiose.

Finally, we should underline that in the largest part of sugars the fusion is associated to the effect 0 DTA, except in the case of anhydrous sugars Cellobiose, Trehalose, Maltose, Inulin, Dextrin, Starch soluble, which melt with the effect I. This fact creates a discrimination between the two kinds of sugars, as far as it shows the different structural stability of their polyhydroxilic frame.

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