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THERMAL INVESTIGATION OF POLYOLS

I. HEXITOLS AND PENTITOLS

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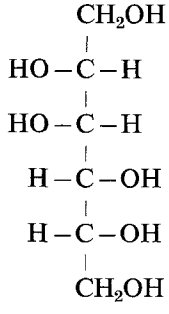
The thermal behaviour of D-mannitol, dulcitol, D-sorbitol, the semihydrate of D-sorbitol, L-arabitol, xylitol and ribitol was investigated by means of differential thermal analysis and a derivatograph. All these polyols are stable up to 200–250°. The endothermic peaks on the DTA curves at lower temperatures are due to melting. These effects are not accompanied by an increase in the electric conductivity. The hexitols decompose endothermally at boiling above 200–250°, the majority of the decomposition products boil out, and the residue is oxidized. The beginning of the decomposition of the pentitols is accompanied by an exothermic peak.

There are very few data in the literature concerning the thermoanalytical properties of polyols. Only the thermal decomposition curve of D-sorbitol is known [1]. For this reason it seemed useful to investigate systematically the behaviour of various polyols on heating. The present paper deals with the thermal investigation of some hexitols: D-mannitol, dulcitol, D-sorbitol (I–III); and pentitols: L-arabitol, ribitol and xylitol (IV–VI). The melting points of these compounds are known (Table 1). D-sorbitol exists as the anhydrous compound [2] (m.p. 92°) and as semihydrate [3] (m.p. 75°). The existence of a third form, the monohydrate, is doubtful [4]. It is noted that D-mannitol sublimes at 130° [6]. Dulcitol, L-arabitol, ribitol used for investigation were supplied by "Chematol", Czechoslovakia. The D-sorbitol was of "clean" grade; the semihydrate was prepared by recrystallization of D-sorbitol from water or alcohol. D-mannitol ("clean for analysis") was recrystallized. The stable modification of xylitol was prepared by recrystallization of the commercial product from water at 45°.



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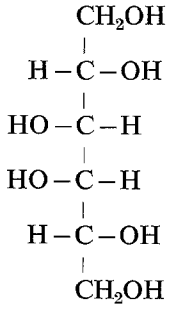

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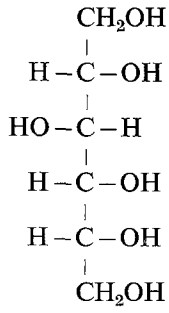

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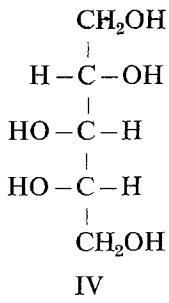

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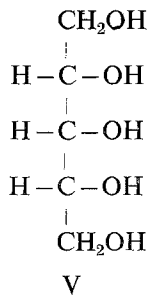

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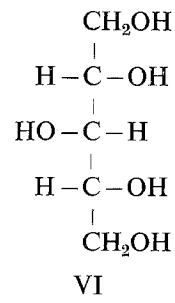

VI

Table 1

Melting points of polyols

Substance	Empirical formula	m.p. °C		Reference
		determined	reported	
D-mannitol	$C_6H_{14}O_6$	166	165.9	[6, 8]
Dulcitol	$C_6H_{14}O_6$	189	189	[7]
D-sorbitol	$C_6H_{14}O_6$	91–93	90	[2]
D-sorbitol, semihydrate	$C_6H_{14}O_6 \cdot 1/2\ H_2O$	75	75	[3]
L-arabitol	$C_5H_{12}O_5$	103	102–103	[8]
Xylitol	$C_5H_2O_5$	91	93–93.5	[10]
Ribitol	$C_5H_{12}O_5$	101	102	[9]

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were taken by means of a Paulik–Paulik–Erdey Derivatograph, using 0.1–0.2 g samples in the smallest platinum crucible. The heating rate was 12° per min, the atmosphere was air, the temperature was measured in the sample, and the reference substance was Al_2O_3. The differential thermal analytical (DTA) and electrical conductivity (TE) curves were taken simultaneously on an NTR-64 apparatus under the same conditions. TG, DTG, DTA and TE curves are presented in common figures (Figs 1–7).

As follows from Figs 1–3, all the hexitols investigated are stable on heating up to 200–250° (240°, 250° and 200° for D-mannitol, dulcitol and D-sorbitol, respectively).

At lower temperatures, only the endothermic minima due to the melting of the substances are observed (165°, 190° and 90° for D-mannitol, dulcitol and D-sorbitol, respectively). Sublimation of D-mannitol at 130° was not observed.

The water of crystallization of the semihydrate of D-sorbitol disappears slowly above the melting temperature (75°) on heating from 160° to 250° (Fig. 4). The melting processes of the hexitols are not accompanied by an increase of the electric conductivity, which indicates the non-ionic nature of the molten substance.

Only the loss of the water of crystallization of the semihydrate of D-sorbitol is accompanied by an increase in the electric conductivity of the sample.

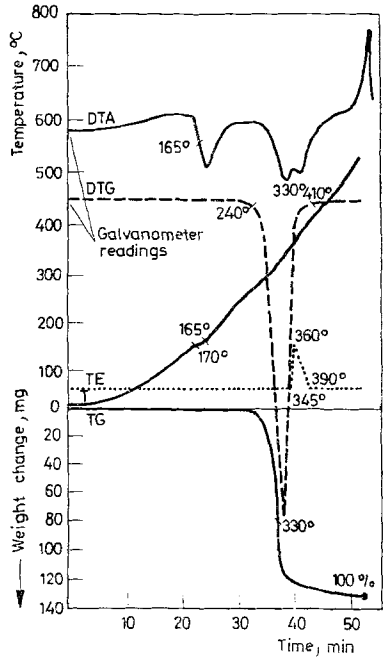

Fig. 1. TG, DTG, DTA and electrical conductivity curves of D-mannitol (Sample weight 130 mg)

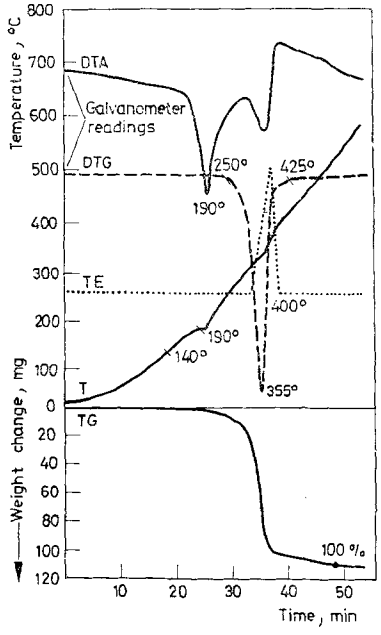

Fig. 2. TG, DTG, DTA and electrical conductivity curves of dulcitol (Sample weight 270 mg)

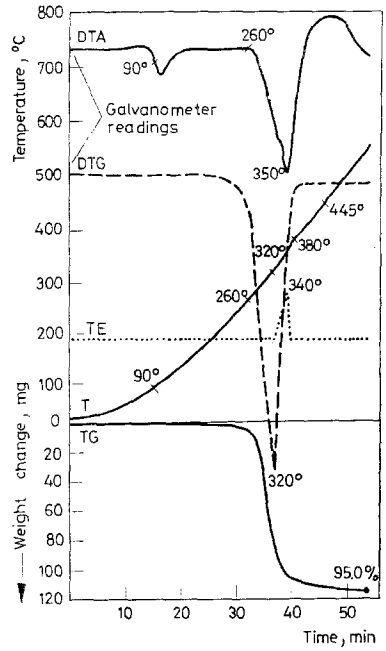

Fig. 3. TG, DTG, DTA and electrical conductivity curves of D-sorbitol (Sample weight 120 mg)

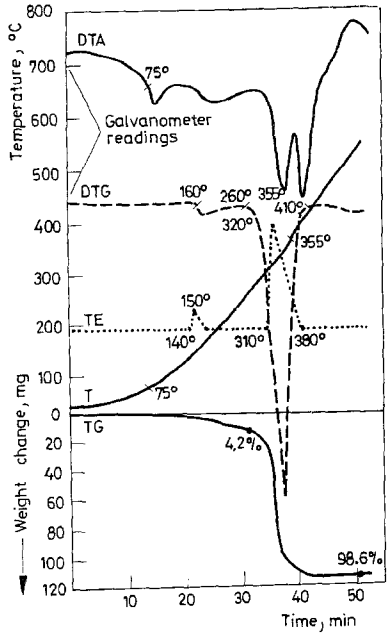

Fig. 4. TG, DTG, DTA and electrical conductivity curves of D-sorbitol semihydrate (Sample weight 125 mg)

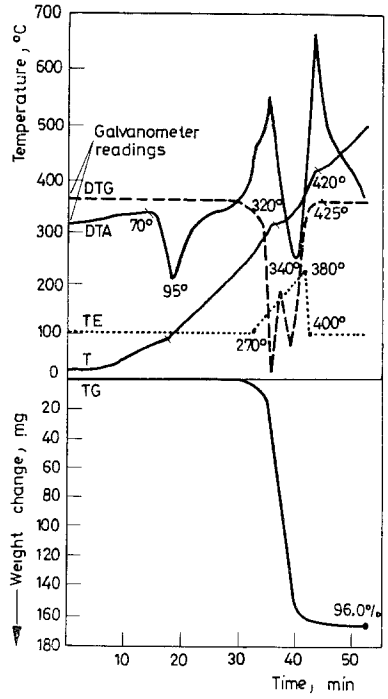

Fig. 5. TG, DTG, DTA and electrical conductivity curves of xylitol (Sample weight 175 mg)

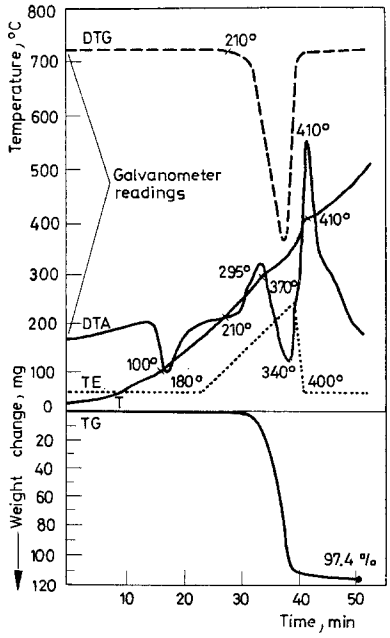

Fig. 6. TG, DTG, DTA and electrical conductivity curves of ribitol (Sample weight 119 mg)

Heating above 200–250° for each compound leads to an endothermic effect on the DTA curve, and a weight loss and extremum on the DTG curve due to the decomposition of the substance and boiling. This process is accompanied by an increase of the electric conductivity. The majority of the decomposition products (~ 90%) boil out, and the residue is oxidized to CO_2 and H_2O in an exothermic reaction (peaks on the DTA curves at 550°, 400° and 440° for D-mannitol, dulcitol and D-sorbitol, respectively).

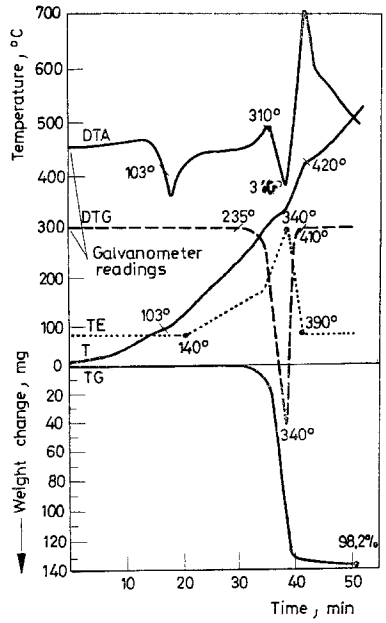

Fig. 7. TG, DTG, DTA and electrical conductivity curves of L-arabitol (Sample weight 140 mg)

The pentitols (see Figs 4–7) were also shown to be stable on heating up to 230° (230°, 230° and 205° for xylitol, ribitol and L-arabitol, respectively). The endothermic minima of melting are observed on the DTA curves at 95°, 104° and 103° for xylitol, ribitol and L-arabitol, respectively.

In contrast to the hexitols the decomposition in this case is accompanied by an exothermic maximum (330°, 300° and 310° for xylitol, ribitol and L-arabitol, respectively).

References

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RÉSUMÉ — On a suivi par ATD et à l'aide d'un derivatograph le comportement thermique des polyalcools suivants: D-mannitol, dulcitol, D-sorbitol, D-sorbitol hémihydraté, L-arabitol, xylitol et adonitol. Tous sont stables jusqu'à 200—250°C. Le pic endothermique qui apparaît sur la courbe d'ATD à plus basse température est dû à la fusion. Celle-ci ne s'accompagne pas d'un accroissement de la conductivité électrique. Les hexitols se décomposent endothermiquement avec ébullition simultanée au-dessus de 200—250° et élimination de la majeure partie des produits de décomposition; le résidu est oxydé. La décomposition des pentitols s'accompagne au début d'un effet exothermique.

ZUSAMMENFASSUNG — Das thermische Verhalten von D-Mannitol, Dulcitol, D-Sorbitol, vom Semihydrat des D-Sorbitol, von L-Arabitol, Xylitol und Ribitol wurde differentialthermoanalytisch und derivatographisch untersucht. Diese Polyole waren bis 200—250° stabil. Die endothermische Spitze der DTA-Kurve bei niedrigerer Temperatur ist dem Schmelzen zuzuschreiben, welches durch kein Erhöhen der elektrischen Leitfähigkeit begleitet ist. Hexitole zersetzen sich endotherm in ähnlicher Weise beim Sieden über 200—250°, der größte Teil der Zersetzungsprodukte entfernt sich und der Rückstand wird oxydiert. Der Zersetzungsbeginn der Pentitole ist von einem exothermen Effekt begleitet.

Резюме — С помощью дериватографа изучено поведение при нагревании Д-маннита, дульцита, Д-сорбита, полугидрата Д-сорбита, L-арабита, ксилита и адонита (рибита). Все эти полиолы устойчивы до 200—250°. Эндотермические минимумы на ДТА ниже этой температуры относятся к плавлению, они не сопровождаются повышением электропроводности. Выше 200—250° гекситы разлагаются эндотермически, большая часть продуктов разложения выкипает, остатки сгорают (экзотермический максимум на ДТА). Разложение пентитов сопровождается экзотермическим эффектом.