Short Communications

THERMAL ANALYSIS OF POLYOLS. II

PENTAERYTHRITOL AND ANALOGOUS COMPOUNDS

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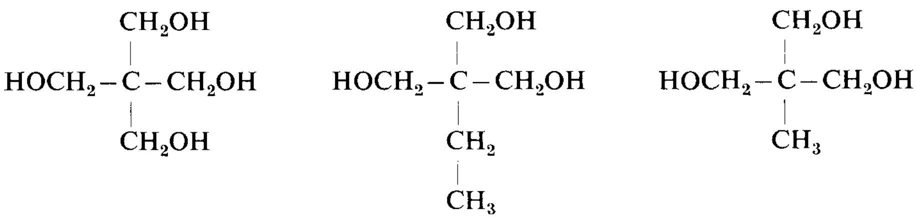
The DTA, TG, DTG and electric conductivity curves of pentaerythritol (I), 1,3-dihydroxy-2-methylol-2-ethylpropane(II) and 1,3-dihydroxy-2-methylol-2-methylpropane(III) have been taken for the first time. Pentaerythritol undergoes a polymorphous change on heating, 1,3-dihydroxy-2-methylol-2-methylpropane forms a syrup in a narrow temperature interval before melting and 1,3-dihydroxy-2-methylol-2-ethylpropane melts with formation of a glass on cooling. The sublimation of substances was also observed.

As a continuation of the thermal analysis of polyols [1], results are reported for pentaerythritol (*I*), 1,3-dihydroxy-2-methylol-2-ethylpropane (*II*) and 1,3-dihydroxy-2-methylol-2-methylpropane (*III*).



I *II* *III*

I crystallizes in the tetragonal system; at 178.1° the crystals change into a polymorphous cubic modification, which melts at 260° [2]. *II* melts at 57–59° [3], and *III* at 190–200.5°, depending on the purity [4–8].

The substances under investigation were prepared and purified as follows: *I* was recrystallized three times from water [9]; *II* was recrystallized three times from ethyl acetate; *III* was prepared according to the procedure described by Ketzlach et al. [8] and purified by recrystallization (three times) from ethyl acetate. The melting points of the pure products were 260°, 60° and 200°, respectively.

The DTA, TG and DTG curves were obtained by means of a Paulik–Paulik–Erdey derivatograph using 0.1–0.2 g samples in the smallest platinum crucible. The heating rates were 12°/min and 3°/min; the cooling curves were also

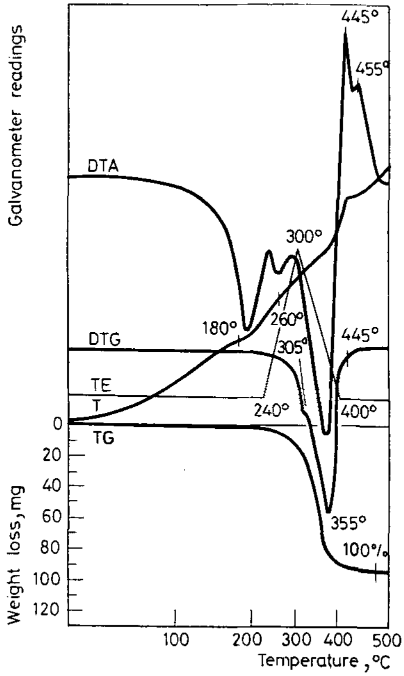


Fig. 1. DTA, TG, DTG and TE curves of pentaerythritol; heating rate 12°/min

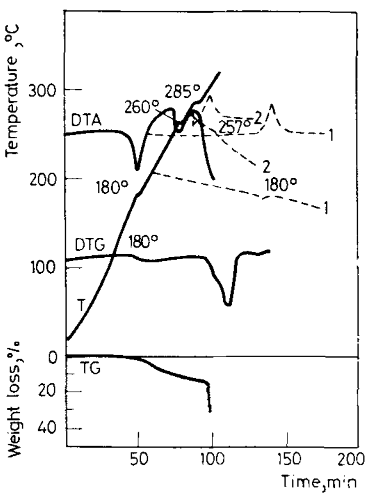


Fig. 2. DTA, TG, DTG and TE curves of pentaerythritol; ——— heating curves (heating rate 3°/min); - - - - cooling curves

taken. The conditions were otherwise the same as previously reported [1]. The DTA and electric conductivity (TE) curves were taken simultaneously on a NTR – 64 apparatus under the same conditions.

The thermal curves of the compounds were taken for the first time (Fig. 1 – 4).

Fig. 1 shows a reversible endothermic minimum at 180° on the DTA curve of *I*, which is independent of the heating rate and is not accompanied by any weight loss. This effect is related to the change to cubic crystal structure. The weight

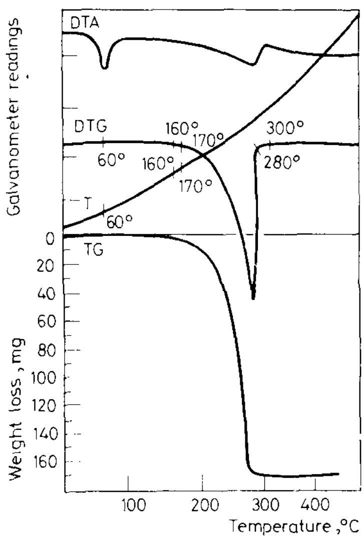


Fig. 3. DTA, TG and DTG curves of 1,3-dihydroxy-2-methylol-2-ethylpropane; heating rate 12°/min

loss at 180 – 260° is due to sublimation. At a heating rate of 3°/min about 15% of the sample sublimes off. At 260° a reversible endothermic minimum is seen; this is associated with an increase of the electric conductivity and is due to melting (Fig. 2). A third endothermic minimum appears at 285 – 290°; this is probably related to boiling and decomposition. Up to 350° almost all the sample (97.7%) is evolved and the residue burns (Fig. 1).

Only an endothermic minimum due to melting is observed on the DTA curve of *II* in the temperature interval 20 – 160° (Fig. 3). This is not associated with any loss of weight or increase of the electric conductivity, but is irreversible, the substance becoming glassy on cooling. The weight loss starts only at 160°. At 200° the sample boils with decomposition, boiling out completely.

The thermal behaviour of *III* was found to be more complex (Fig. 4). The reversible endothermic minimum on the DTA curve at 90°, which is not associated with any increase of electric conductivity or weight loss, is related to the formation of a syrup.

The substance isolated after the completion of the endothermic effect was found to have the same crystallo-optical properties, as the substance isolated at room temperature. At 120° the substance sublimes; 3% is lost in the range 120–200° at a heating rate of 12°/min, and 11% at a heating rate of 3°/min. At 200° a rever-

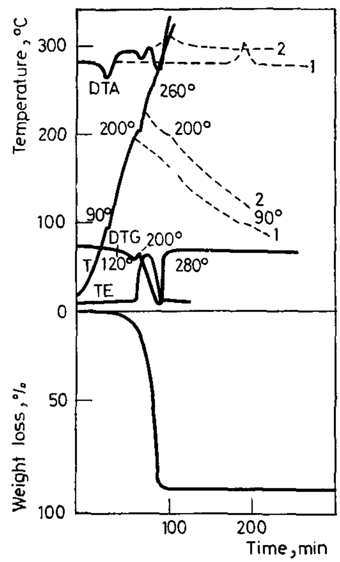


Fig. 4. DTA, TG, DTG and TE curves of 1,3-dihydroxy-2-methylol-2-methylpropane; ——— heating curves (heating rate 3°/min); - - - - cooling curves

sible endothermic minimum, accompanied by an increase of the electric conductivity is observed. This effect is due to melting of the sample. At 260–280° the sample boils out entirely with decomposition.

Hence, in spite of the structural analogy of the compounds investigated, the thermal behaviour of each of them is quite individual and characteristic.

References

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