Journal of Thermal Analysis, Vol. 46 (1996) 1881-1883

Note

COMMENTS ON PENTAERYTHRITOL DSC

W. Balcerowiak

'Blachownia' Institute of Heavy Organic Synthesis, 47–225 Kędzierzyn–Koźle, Poland

(Received October 31, 1995; in revised form February 18, 1996)

Pentaerythritol (2,2-bis-[hydroxymethylene]-1,3-propanediol) is odorless, white, crystalline compound. It usually crystallises in the tetragonal form. At temperatures above 180°C it undergoes a transition from the tetragonal form to a cubic lattice structure. Various melting points have been reported for pure pentaerythritol, with 261–262°C most often mentioned. On heating pentaerythritol sublimes and boils – the temperature dependencies of its vapour pressure have been reported [1, 2].

Owing to such properties, the thermoanalytical curves of pentaerythritol (e.g. TG, DTA or DSC) are strongly affected by the conditions of measurement. Specifically, factors like the heating rate, sample mass, geometry of sample system (sample pan – whether standard or hermetically sealed etc.), purge gas flow rate, the sample grain size distribution and, optionally, the sample dilution are of importance.

The purpose of the present note is to demonstrate the effect of the measurement conditions on the thermal behavior of the sample. With this regard some unusual DSC experiments were performed: in these experiments the sample was not encapsulated, but simple placed in an open sample container. These measurements were carried out in order to study the sublimation behavior of pentaerythritol. In addition, the interpretation given in Ref. [3] has been attempted.

Figure 1 shows DSC curves recorded for pure pentaerythritol, from Fluka AG, using the Mettler TA4000/DSC30 heat-flux differential scanning calorimeter under constant flow of argon (100 ml min^{-1}), at heating rates of 0.5 and 10°C min^{-1}, for sample masses of about 0.5, 2 and 13 mg, in an Al, 40 μl pan,

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

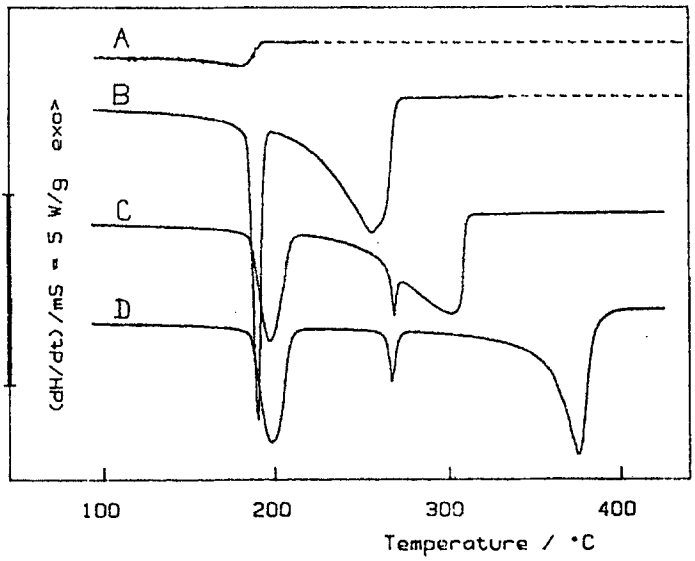

Fig. 1 DSC curves of pure pentaerythritol under dynamic (100 ml min^{-1}) argon atmosphere: A: 0.5°C min^{-1}, 0.425 mg in open pan, B: 10°C min^{-1}, 2.078 mg in open pan, C: 10°C min^{-1}, 12.937 mg in open pan, D: 10°C min^{-1}, 12.933 mg in encapsulated (0.5 mm hole) pan

open or covered (a 0.5 mm hole in the lid). It is clearly seen that a slightest change in any of the measurement conditions above brings about visible or even drastic variations in the shape of the DSC curve for pentaerythritol (the same, pure organic compound!). In the tests carried out with an open pan and a suitably small sample mass and/or low heating rate (i.e. condition 'A'), only sublimation of pentaerythritol from its hexagonal form is observed. With larger sample masses and/or at higher heating rates (i.e. condition 'B'), only a portion of the sample is sublimed before the solid-to-solid transition temperature is reached, after this transformation pentaerythritol of the cubic structure will sublime. Further increase of the sample mass and/or the heating rate will lead to conditions, in which pentaerythritol of the cubic form can reach its melting point, and thus, evaporate after melting (case 'C'). If the pan is capped (by lid with small hole) sublimation and evaporation processes of pentaerythritol are strongly limited at temperatures below its boiling point under atmospheric pressure: the DSC curve will then show only the solid-to-solid transformation, as well as melting and boiling of pentaerythritol (curve 'D'). The above interpretation of the DSC curves of pentaerythritol has been supported by thermogravimetric data obtained under similar conditions (sample mass, pan type, heating rate, gas atmosphere) using the Mettler TA4000/TG50 thermobalance.

DSC curves with some other shapes can also be recorded for pure pentaerythritol when measurement conditions are suitably modified as well. As proved, pentaerythritol is an excellent example of a compound which requires

exact and comprehensive description of the conditions its thermogravimetric measurements are made at, when publishing the obtained data.

Apart from its instructive aspect, the above example shows also that it is not enough to use only 'standard' (for a given laboratory) measurement conditions to extract information necessary to describe the thermal behaviour of a material. From the experience of the author, thermal analysis experiments give interesting and reliable information about the thermal behaviour of materials when they are examined under diverse conditions. Using various sample masses, heating rates and varying between open and crimped pans (with a small hole in the lid) is profitable specifically for low molecular mass organic compounds, despite the procedure is much labour- and time-consuming. Needless to say, the results should always be supported by other, complementary techniques.

References

1 J. Weber and J. Daley, 'Polyhydric Alcohols' in Kirt-Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, New York 1979, Vol. 1, pp. 778–789.
2 E. Barlow, R. H. Berth and J. E. Snow, 'Pentaerythritols', Reinhold Publishing Corporation, New York 1958.
3 F. R. Sale and A. P. Taylor, 'Thermal Analysis – Techniques and Applications', E. L. Charsley, S. B. Warrington (eds.) RSC, Cambridge 1992, p. 212.