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THERMOANALYTICAL EXAMINATION OF ORTHOBORIC ACID

C. Latocha and *M. Uhniat*

"BLACHOWNIA" INSTITUTE OF HEAVY ORGANIC SYNTHESIS,
47–225 KEDZIERZYN-KOŹLE, POLAND

The effects of the conditions of thermal analysis of the process of dehydration of orthoboric acid to boric oxide were studied. The parameters for obtaining structurally arranged boric oxide directly from orthoboric acid were determined.

It is well known that the heating of orthoboric acid causes its dehydration, and metaboric (an intermediate) and boric oxide (the final product) are obtained.

According to the literature data, the dehydration of orthoboric acid starts in the temperature range 55–100° and is completed at approximately 500° [1, 2]. The boric oxide obtained has the form of a glass. Dehydration of orthoboric acid is one of the methods used to manufacture high-purity amorphous boric oxide. One of the two crystalline forms of boric oxide can be obtained from its amorphous form on exposure to the required temperature or to temperature and high pressure [2].

On the basis of the results of thermoanalytical examinations, the present work shows the possibility of obtaining structurally arranged boric oxide by direct dehydration of orthoboric acid.

Experimental

Analytically pure orthoboric acid (ZCh "Tarnowskie Góry") was the subject of our investigation. Experiments were carried out using a Mettler TA–2 thermoanalyzer in an atmosphere of air, at a heating rate of 10 deg min^{-1}. Plate-shaped platinum crucibles (0.075 cm^3) were used.

Results and discussion

Figure 1 shown a comparison of two TG–DTA curves of orthoboric acid. The only difference in the performance of the experiments was that different amounts of

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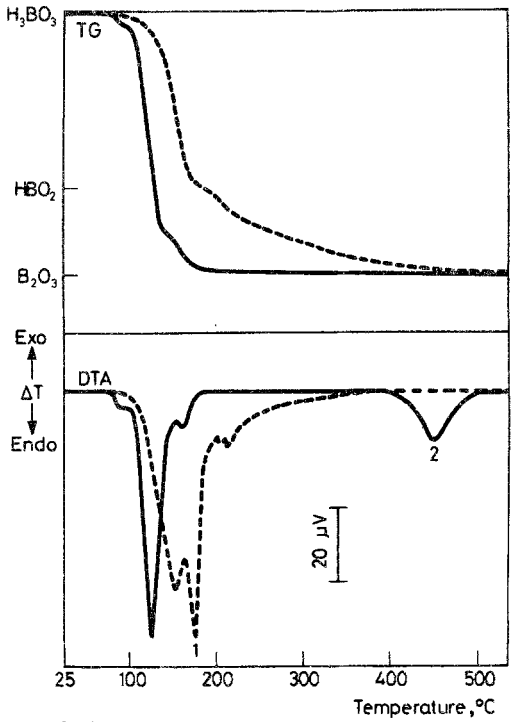

Fig. 1 TG and DTA curves of *o*-boric acid. Full line: m_s = 2.35 mg (NiCr/Ni thermocouples), dashed line: m_s = 37.9 mg (PtRh/Pt thermocouples)

orthoboric acid were used, and thus the sample layer thickness was different in each case. It is easy to see that there are considerable differences between the resulting curves. When a larger orthoboric acid sample having a thickness of approximately 1.0 mm was heated up, the dehydration to boric oxide was completed at a temperature of approximately 500° (Fig. 1, dashed line). Boric oxide was obtained in the form of an amorphous glass. In the DTA curves, no endothermic heat effect is seen which could be responsible for melting of one of the two crystallographic forms of boric oxide: a hexagonal form (mp 450°) or a monoclinic one (mp ca. 510°).

When the sample of boric oxide in the crucible forms a layer with a thickness not exceeding the diameter of a single grain (< 0.1 mm), the TG curve that describes the formation of boric oxide becomes stabilized at approximately 200° (Fig. 1, full line). It was found that the boric oxide obtained in this way had the form of a loose powder. The latter undergoes irreversible melting at a temperaturg which is equivalent to the melting point of the crystalline hexagonal form of boric oxide (peak 2, Fig. 1). Consequently, a structurally arranged boric oxide can be prepared directly from orthoboric acid if a single fundamental condition is met: the

dehydration must be carried out in the solid state, i.e. below the melting temperature of the orthorhombic crystalline form of metaboric acid (mp 176°, peak 1, Fig. 1).

From the described experiments it is seen that the conditions of the dehydration of orthoboric acid (primarily the layer thickness and temperature) are most critical in determining whether a crystalline or an amorphous boric oxide is obtained.

References

1 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam 1963, p. 175.

2 Ullman's Encyclopedia of Industrial Chemistry, VCH, Weinheim-Deerfield Beach 1985, V A4, p. 263.

Zusammenfassung — Der Einfluss der Versuchsbedingungen bei der thermischen Entwässerung von ortho-Borsäure H_3BO_3 zu B_2O_3 wird gezeigt. Die Parameter zur Darstellung von strukturell geordnetem Boroxid direkt aus ortho-Borsäure wurden bestimmt.

Резюме — Изучено влияние экспериментальных условий термического анализа на процесс дегидратации ортоборной кислоты до окиси бора. Из данных для ортоборной кислоты были определены параметры образующегося структурного окружения окиси бора.