



Soviet-era science, translated into English

Reports of the Academy of Sciences of the USSR

V. V. URUSOV

1957

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-195701.53587>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1957. Volume 116, No. 1

CHEMISTRY

V. V. URUSOV

THERMOGRAPHIC INVESTIGATION OF THE DEHYDRATION PROCESS OF ORTHO- BORIC ACID

(Presented by Academician S. I. Vol'fkovich, 22 IV 1957)

There are differing views concerning the course of the process of thermal dehydration of H_3BO_3 to B_2O_3 . This process has been described in the literature both as a two-stage process, in which HBO_2 is formed as an intermediate compound (¹⁻³), and as a three-stage process proceeding with the formation of the intermediate compounds $\text{H}_4\text{B}_2\text{O}_5$ and HBO_2 (⁴), and as a three-stage process in the course of which the intermediate compounds HBO_2 and $\text{H}_2\text{B}_4\text{O}_7$ are obtained (⁵), and as an eight-stage process proceeding through seven intermediate compounds of composition $n\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, where n is equal to from 1 to 8 (⁶).

However, of all the intermediate compounds listed, only metaboric acid has been studied in detail, has been recognized as a chemical individual, and is currently known in three modifications, monotropic with respect to one another (⁷); the existence of the others remains in question.

In the present work, the results of a renewed investigation of the process of thermal dehydration of H_3BO_3 , carried out by the thermographic method, are briefly presented.

Dehydration was carried out by heating the acid in Stepanov glass vessels (⁸) at a rate of 1-2° per minute, at the following prescribed values of external pressure: 740, 600, 500, 400, 300, 200, 100, 75, 65, 50, 25, 20, 15, and 10 mm Hg. From the thermograms obtained it was established that the course of this process has a different character depending on the value of the applied external pressure. One-stage, two-stage, and three-stage pathways of dehydration of H_3BO_3 were observed.

When H_3BO_3 is heated under pressures from 740 to 65 mm Hg, its dehydration proceeds as a two-stage process, with the formation of HBO_2 III* as an interme-

Fig. 1. Thermograms of orthoboric acid at different pressures (mm Hg): a—100, b—50, c—15, d—10

Figure 1: Fig. 1. Thermograms of orthoboric acid at different pressures (mm Hg): a—100, b—50, c—15, d—10

diate compound, which is reflected in the thermograms as two clearly expressed endothermic effects (Fig. 1, *a*).

The first effect on such thermograms corresponds to the course of dissociation of H_3BO_3 into HBO_2 III and water vapor at a temperature from 149 to 101° —depending on the value of the specified external pressure. The second effect on them is due to the melting of HBO_2 III at 176° , if the heating of H_3BO_3 is carried out under a pressure of 740 mm Hg. When H_3BO_3 is heated under a pressure of 600 mm Hg and below, this effect corresponds to the course of partial dehydration of HBO_2 III with the formation of a solution at a temperature from 175 to 147° , depending on the pressure.

The solutions formed as a result of the processes corresponding to the second effect, during their further heating, boil away without separation of a solid phase from them, which leads to the production of a melt of B_2O_3 . The process of boiling away of the solutions is not clearly reflected on the thermograms.

* III—the third modification.

The observed dissociation pressure of H_3BO_3 into HBO_2 III and water vapor as a function of temperature is presented in coordinates $\log p - \frac{1}{T}$ in Fig. 2 by segment *AB*. As shown in the same figure, it proved to be practically equal to the equilibrium pressure measured by several authors by the static method under isothermal conditions ^(3,7).

When the dehydration of H_3BO_3 is conducted under a pressure of 50 – 15 mm Hg, it proceeds as a three-stage process with the formation, as intermediate compounds, of HBO_2 and a second hydrate compound or solid solution, which is reflected on the thermograms in the form of three clearly expressed endothermic effects (Fig. 1, *b*).

Fig. 1. Thermograms of orthoboric acid at different pressures (mm Hg): *a*— 100 , *b*— 50 , *c*— 15 , *d*— 10

The first effect on such thermograms is due to the course of dissociation of H_3BO_3 into HBO_2 and water vapor at temperatures from 96 to 83° , depending on the magnitude of the imposed external pressure. The second effect corresponds to the dissociation of HBO_2 into a second intermediate hydrate compound or solid solution and water vapor, which occurs at temperatures from 143 to 112° , depending on the magnitude of the imposed external pressure. The third effect is due to the course of dissociation of the second hydrate compound

Fig. 2

Figure 2: Fig. 2

or solid solution into amorphous B_2O_3 and water vapor at 144-150°, if the heating of H_3BO_3 is carried out under a pressure of 25 mm Hg and below. When H_3BO_3 is heated under a pressure of 50 mm Hg, this effect corresponds to the course of partial dehydration of the second hydrate compound or solid solution at 154°, with the formation of a liquid solution, which during further heating boils away without separation of a solid phase from it, leading to the formation of a melt of B_2O_3 . The boiling of the solution is not clearly reflected on the thermograms.

The dissociation pressure of orthoboric acid into HBO_2 and water vapor observed in the three-stage dehydration process as a function of temperature is presented in Fig. 2 by segment BD . It proved to be lower than the equilibrium pressure known from the literature ^(3,7) in the system H_3BO_3 — HBO_2 III—vapor, shown as a function of temperature in the same figure by segment BC . This phenomenon is most probably due to the formation, during dehydration of H_3BO_3 under a pressure of 50-15 mm Hg,

initially HBO_2 with an unstable pseudostructure, as a result of which, in the thermographic investigation, the pressure was measured in the system H_3BO_{3st} — HBO_{2unst} —vapor, and not in the system H_3BO_{3st} — HBO_2 III_{st}—vapor.

It may be assumed that HBO_2 with an unstable pseudostructure was transformed into a second hydrated compound or a solid solution and water vapor without preliminary rearrangement of its crystal lattice, since the exothermic effect corresponding to this process was not observed on the thermograms. The observed dissociation pressure of HBO_2 as a function of temperature is represented in Fig. 2 by the segment EF .

Fig. 2. Dependence of the dissociation pressures of orthoboric and metaboric acids on temperature. ABC —dissociation of H_3BO_3 to HBO_2 in the form of the third modification and $H_2O(g)$; BD —dissociation of H_3BO_3 to HBO_2 of the presumed unstable structure and $H_2O(g)$; EF —dissociation of HBO_2 of the presumed unstable structure to a hydrated compound or solid solution and $H_2O(g)$.

1—our data; 2—data of (3, 7), etc.

The second hydrated compound or solid solution obtained in the experiments, with a B_2O_3 content from 80.4 to 82.2%, does not correspond in composition to any of the above-mentioned intermediate compounds described in the literature.

When H_3BO_3 is heated under a pressure of 15 mm Hg, its dehydration may proceed partly in the form of the described three-stage process and partly as a single-stage process. This phenomenon was observed in several experiments, being reflected on the thermograms in the form of five endothermic effects (Fig.

1, c). The first effect on such thermograms corresponded to the dissociation of H_3BO_3 into HBO_2 and water vapor, beginning at 83° and proceeding at first at a rate sufficient for it to be reflected in the record of the simple thermocouple as a horizontal plateau, and then ceasing or sharply slowing down; as a result, the mixture of H_3BO_3 with HBO_2 that formed gradually heated to a temperature of 98° , at which a second process arose, corresponding to the second effect on the thermograms. The second process consisted in the dissociation of H_3BO_3 into amorphous B_2O_3 and water vapor. It proceeded, being reflected in the record of the simple thermocouple also as a horizontal plateau, and was interrupted in connection with the renewed rapid course of the first process, which led to a lowering of the temperature of the mixture of H_3BO_3 , HBO_2 , and B_2O_3 formed to 83° and caused the appearance of the third effect on the thermograms. The fourth and fifth effects on

in the thermograms corresponded to the dissociation of HBO_2 into a second intermediate hydrate compound or a solid solution and water vapor at 112° , and to the dissociation of the second intermediate hydrate compound or solid solution into amorphous B_2O_3 and water vapor at 144° .

When the dehydration of H_3BO_3 is conducted under a pressure of 10 mm Hg, it proceeds as a single-stage process, representing the dissociation of H_3BO_3 directly into amorphous B_2O_3 and water vapor, occurring at $96\text{--}98^\circ$ and appearing on the thermograms as a clearly expressed endothermic effect (Figs. 1, 2). This process indicates the existence in the $\text{B}_2\text{O}_3\text{--H}_2\text{O}$ system of a eutectic, not yet found, formed by orthoboric acid and boric anhydride.

The discovered pathways of dehydration of H_3BO_3 , along which it proceeds at an external pressure of 10–25 mm Hg, may be of practical interest, since they make it possible to avoid melting in the production of boric anhydride from orthoboric acid, using a less deep vacuum in comparison with those previously proposed, with a residual pressure of 1–2 mm Hg.⁽⁹⁾ and 13–15 mm Hg.⁽¹⁰⁾

Scientific Institute for Fertilizers
and Insectofungicides
named after Ya. V. Samoilov

Received
15 IV 1957

CITED LITERATURE

- ¹ H. Menzel, H. Schulz, H. Deckert, *Z. anorg. Chem.*, **220**, 49 (1934).
- ² M. Stackelberg, F. Quatram, J. Dressel, *Zs. Electrochem.*, **43**, 14 (1937).
- ³ H. Tazaki, *J. Sci. Hirosima Univ.*, Ser. A, **10**, 37, 55, 63, 109, 113 (1940).
- ⁴ A. B. Nikolaev, *Physicochemical Study of Natural Borates*, Publishing House of the USSR Academy of Sciences, 1947, p. 136.
- ⁵ A. Thiel, H. Siebeneck, *Zs. anorg. allgem. Chem.*, **220**, 236 (1934).
- ⁶ L. F. Gilbert, M. Levi, *J. Chem. Soc.*, **1**, 527 (1929).

- ⁷ F. C. Kracek, G. W. Morey, H. E. Merwin, *Am. J. Sci.*, **35A**, 143 (1938).
⁸ L. G. Berg, A. V. Nikolaev, E. Ya. Rode, *Thermography*, Publishing House of the USSR Academy of Sciences, 1944, p. 54.
⁹ E. Tiede, A. Ragoss, *Ber.*, **56**, 656 (1923).
¹⁰ V. N. Krylov, Author' s Certificate No. 61900 of 19/IV 1941, class 12i, 40.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.