*Journal of Thermal Analysis, Vol. 1 (1969) 279—283*

# THERMAL DECOMPOSITION OF SOME HEXABORATES

E. SCHWARTZ, A. DZENE and A. IEVIŅŠ

*Institute of Inorganic Chemistry, Riga, U.S.S.R.*

(Received March 27, 1969)

Thermal decomposition of iron(II) and cobalt(II) hexaborates has been investigated. The methods applied to investigate the process were differential thermal analysis, derivatography, crystallooptics and x-ray study. The following iron(II) hexaborate hydrates, $FeO \cdot 3B_2O_3 \cdot 7.5H_2O$, $FeO \cdot 3B_2O_3 \cdot 5H_2O$, $FeO \cdot 3B_2O_3 \cdot 0.5H_2O$; iron(III) borates, $Fe_2O_3 \cdot 6B_2O_3$ and $2Fe_2O_3 \cdot B_2O_3$; cobalt(II)hexaborate hydrates $CoO \cdot 3B_2O_3 \cdot 7.5H_2O$, $CoO \cdot 3B_2O_3 \cdot 5H_2O$, $CoO \cdot 3B_2O_3 \cdot 0.5H_2O$, $CoO \cdot 3B_2O_3$ and the decomposition product $2CoO \cdot 3B_2O_3$ have been isolated. Hepta- and semihydrates of cobalt(II) and iron(II) hexaborates have been proved to be isomorphous. It has been established that in the case of cobalt and iron hexaborates the exothermic maximum refers to a decomposition reaction and to the formation of a borate containing a smaller proportion of boron and boric anhydride.

In the present paper the thermal decomposition of iron(II) and cobalt(II) hexaborates is described. Intermediates and final products of thermal decomposition were isolated and identified by means of chemical analysis, optical study of crystals, and by taking the corresponding debayegrams (Fe-radiation). Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were taken by means of the F. Paulik, J. Paulik, L. Erdey Derivatograph [1] using $0.1-0.2$ g samples at a heating rate of 12° per minute. Differential thermal analysis (DTA) and electrical conductivity (TE) curves were taken by an FPK-59 apparatus simultaneously at the same rate of heating [2]. TG, DTG, DTA and TE curves are presented in common figures (Figs 1 and 2). Optical indexes of crystals were determined by means of the immersion method.

Iron(II) and cobalt(II) hexaborates were synthesized according to methods given in references [3, 4]; their analysis was carried out as follows: $B_2O_3$ was determined according to [5], CoO complexometrically, Fe(II) by titration with potassium permanganate, and Fe(III) by reduction with ascorbic acid, the excess of the latter being titrated iodometrically. The water of crystallization was determined volumetrically by means of lithium hydride [6] using L. Berg's automatic burette. By stopping the heating of the sample in the derivatograph furnace at temperatures where the separate dehydration stages ended, intermediate hydrates were isolated. Likewise the intermediates of decomposition formed directly before as well as after the "borate regrouping" were also isolated. The properties

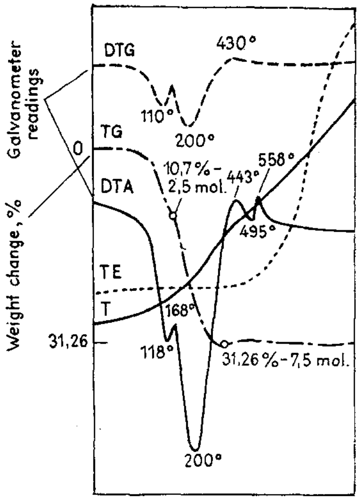


Fig. 1. Derivatogram of $FeO \cdot 3B_2O_3 \cdot 7.5H_2O$

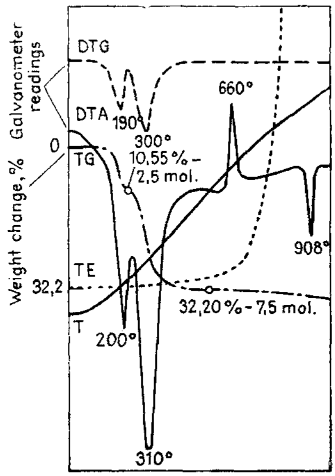


Fig. 2. Derivatogram of $CoO \cdot 3B_2O_3 \cdot 7.5H_2O$

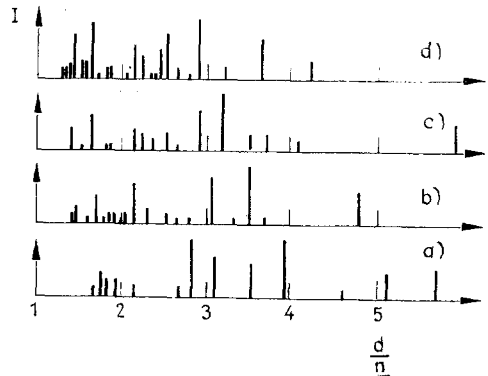


Fig. 3. Debayegrams of the dehydration and thermal decomposition products of iron(II) hexaborates. *a)* $FeO \cdot 3B_2O_3 \cdot 7.5H_2O$, *b)* $FeO \cdot 3B_2O_3 \cdot 5H_2O$; *c)* $Fe_2O_3 \cdot 6B_2O_3$, *d)* $2Fe_2O_3 \cdot B_2O_3$

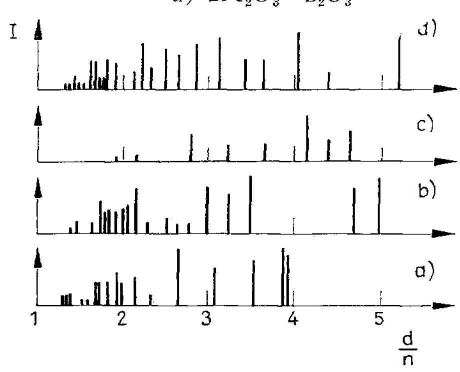


Fig. 4. Debayegrams of the dehydration and thermal decomposition products of cobalt(II) hexaborates. *a)* [$CoO \cdot 3B_2O_3 \cdot 7.5H_2O$, *b)* $CoO \cdot 3B_2O_3 \cdot 5H_2O$; *c)* $CoO \cdot 3B_2O_3$' *d)* $3CoO \cdot 3B_2O_3$

Table 1

Composition and properties of hydrates and other products of the thermal decomposition of iron(II) hexaborate

| Substance | t° of formation | Composition, % | | | | | | Ng | Np | $d^{\circ}_{25}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | FeO or $Fe_2O_3$ | | $B_2O_3$ | | $H_2O$ | | | | |
| | | calc. | found | calc. | found | calc. | found | | | |
| $FeO \cdot 3B_2O_3 \cdot 7.5H_2O$ | 20° | 17.28 | 17.38 | 50.23 | 50.13 | 32.49 | 32.15 | 1.514 | 1.475 | 2.09 |
| $FeO \cdot 3B_2O_3 \cdot 5H_2O$ | 168° | 19.37 | 19.10 | 56.34 | 56.36 | 24.29 | 23.95 | 1.534 | 1.471 | 2.12 |
| $FeO \cdot 3B_2O_3 \cdot 0.5H_2O$ | 300° | 24.79 | 24.54 | 72.10 | 72.03 | 3.11 | 3.74 | amorphous | | 2.14 |
| $Fe_2O_3 \cdot 6B_2O_3$ | 500° | 27.65 | 27.01 | 72.35 | 72.23 | — | — | 1.642 | 1.587 | 2.15 |
| $2Fe_2O_3 \cdot B_2O_3$ | 950° | 82.10 | 81.74 | 17.90 | 18.06 | — | — | >2.05 | >2.05 | 2.33 |

Table 2

Composition and properties of hydrates and other products of the thermal decomposition of cobalt(II) hexaborate

| Substance | t° of formation | Composition, % | | | | | | Ng | Np | $d^{\circ}_{25}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | CoO | | $B_2O_3$ | | $H_2O$ | | | | |
| | | calc. | found | calc. | found | calc. | found | | | |
| $CoO \cdot 3B_2O_3 \cdot 7.5H_2O$ | 25° | 17.89 | 17.79 | 49.86 | 49.55 | 32.25 | 32.20 | 1.517 | 1.470 | 1.98 |
| $CoO \cdot 3B_2O_3 \cdot 5H_2O$ | 250° | 20.04 | 20.30 | 55.87 | 55.22 | 24.09 | 24.40 | 1.556 | 1.480 | 2.18 |
| $CoO \cdot 3B_2O_3 \cdot 0.5H_2O$ | 550° | 25.59 | 25.55 | 71.33 | 71.02 | 3.08 | 2.48 | amorphous | | 2.29 |
| $CoO \cdot 3B_2O_3$ | 600° | 26.40 | 26.10 | 73.60 | 74.09 | — | — | 1.518 | 1.498 | 2.34 |
| $2CoO \cdot 3B_2O_3$ | 900° | 58.23 | 57.95 | 41.77 | 41.86 | — | — | 1.645 | 1.569 | 3.33 |

of all the above-mentioned products are shown in Tables 1 and 2; debayegrams are given in Figs 3 and 4.

Iron(II) and cobalt(II) hexaborates were proved to be isomorphous and to have the composition $MeO \cdot 3B_2O_3 \cdot 7.5H_2O$, although formerly the compounds were supposed to have eight molecules of water of crystallization. By heating the compounds, it was established that crystalline pentahydrates, $MeO \cdot 3B_2O_3 \cdot 5H_2O$, are first formed, and afterwards amorphous semihydrates, $MeO \cdot 3B_2O_3 \cdot 0.5H_2O$. The last half molecule of water disappears slowly: from iron(II) hexaborate above 443°, together with the oxidation of iron; from cobalt(II) hexaborate at 600°.

There are two exothermic maxima on the DTA curve of iron(II) hexaborate, at 443° and at 558°. The one at 443° refers to the oxidation of iron(II) to iron(III). On the DTA curve of cobalt(II) hexaborate there is only one exothermic maximum, at 650°. Up to now these effects were supposed to belong to "borate regrouping", i.e. the transformation of amorphous borate (the product of dehydration) to a crystalline form. However, amorphous iron(II) hexaborate is formed at 300°, but cobalt(II) hexaborate at 550°; at 500°, i.e. just before the "borate regrouping", a crystalline iron(III) borate (Ng = 1.642, Np = 1.587 debayegram in Fig. 3), $Fe_2O_3 \cdot 6B_2O_3$ is formed; at 600°, a crystalline cobalt(II) borate, $CoO \cdot 3B_2O_3$ (Ng = 1.518, Np = 1.498, debayegram in Fig. 4) was isolated. These exothermic effects, in the case of iron(III) hexaborate as well as in that of cobalt(II) hexaborate, have been proved to be accompanied by the increase of electrical conductivity of the sample. After the exothermic peak a mixture of crystals of cobalt(II) borate or iron(III) borate containing a smaller proportion of boron with white crystals (Ng = 1.464, Np 1.408) is formed. This is supposed to be boric acid formed from boric anhydride during the cooling of the sample in the air. It was possible to wash off the excess of boric acid by multiple evaporation of the thermal decomposition products in methyl alcohol until constant weight was attained. Finally the borates $2Fe_2O_3 \cdot B_2O_3$ (Ng and Np > 2.05) and $2CoO \cdot 3B_2O_3$ (Ng = 1.645, Np = 1.569) were isolated.

Thus, the exothermic effect at 558° in the case of iron(III) hexaborate refers to the exothermal decomposition reaction:

$$2(Fe_2O_3 \cdot 6B_2O_3) \rightarrow 2Fe_2O_3 \cdot B_2O_3 + 11B_2O_3$$

whereas the exothermic effect at 650° in the case of cobalt(II) hexaborate refers to the reaction:

$$2(CoO \cdot 3B_2O_3) \rightarrow 2CoO \cdot 3B_2O_3 + 3B_2O_3.$$

## References

1. F. Paulik, J. Paulik, L. Erdey, Z. anal. Chem., 160 (1958) 241.
2. L. Berg, N. Burmistrova, Rep. II Conferences on Thermography, Kazan, 1961, p. 125.
3. A. Kešāns, S. Vimba, Izv. AN Latv. SSR, 1953, N 3, 123.
4. E. Schwartz, A. Ieviņš, Zhurnal Neorg. Khim., 5 (1960) 1617.
5. E. Schwartz, A. Dzene, A. Ieviņš, Izv. AN Latv. SSR, Ser. khim. 1968, N 6, 749.
6. L. Berg, Introduction into Thermography, Moscow, 1961, p. 251.

RÉSUMÉ. — On a étudié la décomposition thermique des hexaborates de fer-II et de cobalt-II, par analyse thermique différentielle, dérivatographie, cristallo-optique et rayons X. Les hexaborates de fer-II hydratés suivants ont pu être isolés: $FeO \cdot 3B_2O_3 \cdot 7.5H_2O$, $FeO \cdot 3B_2O_3 \cdot 5H_2O$, $FeO \cdot 3B_2O_3 \cdot 0.5H_2O$ ainsi que les borates de fer-III $Fe_2O_3 \cdot 6B_2O_3$ et $2Fe_2O_3 \cdot B_2O_3$, les hexaborates hydratés de cobalt $CoO \cdot 3B_2O_3 \cdot 7.5H_2O$, $CoO \cdot 3B_2O_3 \cdot 5H_2O$, $CoO \cdot 3B_2O_3 \cdot 0.5H_2O$ et $CoO \cdot 3B_2O_3$ et le produit de décomposition $2CoO \cdot 3B_2O_3$. On a montré que les hexaborates hepta et hémihydratés de fer-II et de cobalt-II étaient isomorphes. Le maximum exothermique des hexaborates de fer et de cobalt correspond à une réaction de décomposition où un borate d'une teneur moindre en bore et en acide borique anhydre apparaît.

ZUSAMMENFASSUNG. — Es wurde die thermische Zersetzung der Eisen(II)- und Kobalt(II)-hexaborate untersucht. Folgende Methoden wurden angewandt: differentiale Thermoanalyse, Derivatographie, Kristalloptik und Röntgenographie wobei folgende Verbindungen isoliert werden konnten: $FeO \cdot 3B_2O_3 \cdot 7.5H_2O$; $FeO \cdot 3B_2O_3 \cdot 5H_2O$, $FeO \cdot 3B_2O_3 \cdot 0.5H_2O$, $Fe_2O_3 \cdot 6B_2O_3$; $2Fe_2O_3 B_2O_3$; $CoO \cdot 3B_2O_3 \cdot 7.5H_2O$; $CoO \cdot 3B_2O_3 \cdot 5H_2O$, $CoO \cdot 3B_2O_3 \cdot 0.5H_2O$, $CoO \cdot 3B_2O_3$ und das Zersetzungsprodukt $2CoO \cdot 3B_2O_3$. Die Hepta- und Semihydrate der Eisen(II)- und Kobalt(II)hexaborate zeigten sich isomorph. Das exothermische Maximum bei den Eisen- und Kobalthexaboraten entspricht einer Zersetzungsreaktion, wobei ein Borat entsteht, welches weniger Bor oder Borsäureanhydrid enthält.

Резюме. — Исследован термораспад гексабората железа(2) и кобальта(2). Для изучения процесса распада пользовались методом дериватографии, кристалло-оптики и диффракции рентгеновских лучей. Выделены следующие гидраты гексабората железа (2) и бораты железа(3), соответственно: $FeO \cdot 3B_2O_3 \cdot 7,5H_2O$, $FeO \cdot 3B_2O_3 \cdot 5H_2O$, $FeO \cdot 3B_2O_3 \cdot 0,5H_2O$, $Fe_2O_3 \cdot 6B_2O_3$ и $2Fe_2O_3 \cdot B_2O_3$. Изолированы следующие гидраты гексабората кобальта: $CoO \cdot 3B_2O_3 \cdot 7,5H_2O$, $CoO \cdot 3B_2O_3 \cdot 5H_2O$, $CoO \cdot 3B_2O_3 \cdot 0,5H_2O$, $CoO \cdot 3B_2O_3$ и продукт распада $2CoO \cdot 3B_2O_3$. Гепта- и полугидраты гексаборатов кобальта(2) и железа(2) оказались изоморфными. Установлено, что в случае гексаборатов кобальта и железа экзотермический максимум соответствует реакции распада и образованию бората, содержащего меншее количество бора, и окиси бора.