THERMAL DECOMPOSITION OF LITHIUM PEROXOBORATE

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It was indicated in [1-3] that in the case of the decomposition of NaBO$_3$·H$_2$O, part of the peroxide oxygen is retained in the substance, losing its peroxide nature. In this case the substance becomes paramagnetic. A detailed study was made of the kinetics of the decomposition of NaBO$_3$·H$_2$O. As a result of the decomposition, a substance with the composition NaBO$_3$·8 was obtained [4].* Such an unusual nature of the decomposition of the peroxide compound, leading to the production of an oxygen-rich substance, the nature and chemical properties of which are still obscure, is of interest for the chemistry of boron and peroxides. This work presents the results of an investigation of the thermal decomposition of LiBO$_3$·H$_2$O.

EXPERIMENTAL METHOD

Lithium peroxoborate was produced according to the method of [5]. The decomposition was conducted at 120-280° under vacuum, freezing out the H$_2$O formed. At the end of the experiment, according to the data of analysis, as well as the weight loss of the substance, the weight of H$_2$O in the condenser and the increase in the pressure in the system were calculated; $\Delta$ is the total degree of conversion of peroxide oxygen, equal to the ratio of decomposed O$_2^-$ to the initial amount, g; $\Delta_1$ is the degree of conversion of O$_2^-$ to pseudo-superperoxide oxygen; $\Delta_2$ is the degree of conversion of O$_2^-$ to oxygen liberated in the form of a gas; $\Delta_{H_2O}$ is the degree of dehydration.

Table 1 presents the results of certain experiments, while Fig. 1 gives the dependences of $\Delta_1$, $\Delta_2$, and $\Delta_{H_2O}$ on the total degree of conversion $\Delta$ at all the temperatures studied.

Just as in the case of NaBO$_3$·H$_2$O, in the decomposition of LiBO$_3$·H$_2$O part of the oxygen remains in the substance, while part is liberated into the gas phase. The process is also accompanied by an evolution of H$_2$O. The composition of the solid phase is practically independent of the temperature, but is a function of the degree of conversion of peroxide oxygen, and therefore it is impossible to significantly influence the

*The nature of this compound is as yet unknown; following the authors of [2], we shall call it a pseudosuperoxide, and the oxygen superpseudoperoxide oxygen, denoted by the symbol $(O_2)_{ps}$.

Fig. 1. Dependence of $\Delta_1$ (1), $\Delta_2$ (2), and $\Delta_{H_2O}$ (3) on the total degree of conversion $\Delta$ at the temperature, °C: a) 115; b) 120; c) 125; d) 135; e) 140; f) 145.


TABLE 1. Results of Certain Experiments on the Decomposition of 
LiBO₃·H₂O Composition, %: Li₂O 16.8; B₂O₃ 41.7; O₃⁻ 21.0; H₂O 20.7. 
Sample Weight ~0.4 g

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<tr>
<th>T, °C</th>
<th>t, min</th>
<th>Content, %</th>
<th>Degree of conversion, o/°</th>
<th>Δi/Δf</th>
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<td></td>
<td>O₂⁻</td>
<td>(O₂)ₚₛ</td>
<td>Δ₁</td>
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* Decomposition of NaBO₃·H₂O [4].

direction of the decomposition by varying the temperature (see Fig. 1). However, the ratio of various characteristics and the development of the process with time substantially distinguishes the decomposition of LiBO₃·H₂O from that of NaBO₃·H₂O.

In the decomposition of LiBO₃·H₂O, the conversion of O₂⁻ outstrips the evolution of H₂O, especially at small Δ. After Δ reaches 50%, the rate of evolution of H₂O increases, but nonetheless when Δ = 80-85%, ΔH₂O = 45%, and the gross composition of the substance is LiBO₂·0.5H₂O. The removal of 0.5 mole of water occurs only above 200°. The composition of the substance formed is LiBO₂.ₖ. Let us recall that in the decomposition of NaBO₃·H₂O during the entire process ΔH₂O lagged only slightly behind Δ, It is also characteristic of LiBO₃·H₂O that as the decomposition proceeds, the ratio Δ₁/Δ₂ varies from 8-10 to ~1.

At the beginning of the process (up to Δ ~ 40%), almost all of the oxygen is retained in the solid phase. Then the content of (O₂)ₚₛ increases extremely negligibly, reaching 11-13%, while the amount of oxygen liberated, characterized by Δ₂, increases sharply, reaching 50% when Δ = 100%. In other words, the decomposition of peroxide oxygen is described by the scheme:

\[
\begin{align*}
\text{O}_2^{-} & \xrightarrow{\Delta = 40\%} \text{(O}_2\text{)}_{\text{ps}} \\
\Delta & \geq 40\% \xrightarrow{} \text{(O}_2\text{)}_{\text{f}}
\end{align*}
\]

The second direction of the process is also accompanied by a substantial removal of H₂O. For the decomposition of O₂⁻ we determined the activation energy E = 46 kcal/mole (at Δ = 40-50%). For Na, E = 36 kcal/mole. As a result of the different temperature coefficients, the decomposition of LiBO₃·H₂O up to 140° proceeds more slowly than the decomposition of NaBO₃·H₂O, while above 140° it is more rapid. The decomposition products, like the initial LiBO₃·H₂O, are x-ray amorphous. The structure of LiBO₃·H₂O is unknown. By analogy with NaBO₃·H₂O we can assume that the anion has the structure:

\[
\begin{align*}
\text{OH} & \quad \text{O} \quad \text{OH} \\
\text{B} & \quad \text{O} \quad \text{B} \\
\text{OH} & \quad \text{O} \quad \text{OH}
\end{align*}
\]

From the data obtained it follows that the B–OH bond in peroxoborates is substantially stronger than the bond in (O–O)²⁻ and B–OH in NaBO₃·H₂O. This may explain the different behavior of Li and Na peroxoborates during decomposition. It is also probable that steric factors have a significant influence on the conversion O₂⁻→(O₂)ₚₛ.

CONCLUSIONS

In the case of the decomposition of LiBO₃·H₂O under vacuum in the interval 115-145°, 50% of the oxygen is retained in the solid phase, while 50% is liberated in the form of O₂. In this case 0.5 mole H₂O is