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Abstract

Full Text

Chemistry

L. V. Titov

Synthesis of Calcium Borohydride

(Presented by Academician N. M. Zhavoronkov, July 19, 1963)

Calcium borohydride, $Ca(BH_4)_2$, along with the borohydrides of alkali metals, can be used for selective reduction in aqueous solutions; in the case of reduction of substances that do not tolerate an alkaline medium, for example sugars, it even has an advantage over sodium and potassium borohydrides. Calcium borohydride can also be successfully used for the synthesis of boranates of other metals and organic bases by reaction with sulfates of these bases, for example,

$$Me_2SO_4 + Ca(BH_4)_2 \rightarrow 2MeBH_4 + CaSO_4.$$

Synthesis of calcium borohydride has been described only in the works of Kollonitsch et al. ([1,2]), but without indication of the degree of purity of the preparation. According to these works, calcium borohydride is obtained by the reaction of sodium borohydride with anhydrous calcium chloride in ethyl alcohol ([1])—at negative temperatures, or tetrahydrofuran (THF)—at room temperature ([2]). The main difficulty in developing methods for obtaining borohydrides, and in particular calcium borohydride, in the pure state by exchange reactions is the lack of data on the solubility of the starting substances and reaction products in organic solvents. For this reason, synthetic work must be combined with the obtaining of new solubility data.

Fig. 1. Solubility polytherm of calcium borohydride in tetrahydrofuran: *a*—data of the visual-polythermal method, *b*—data of the solubility method.

In choosing pyridine as the solvent for carrying out the reaction

$$CaCl_2 + 2NaBH_4 \rightarrow Ca(BH_4)_2 + 2NaCl \quad (1)$$

we proceeded from the good solubility in it of sodium borohydride ([3]), the

Fig. 2. Heating curves of calcium borohydride: simple (1) and differential (2), combined with the hydrogen-evolution curve (3)

Figure 2: Fig. 2. Heating curves of calcium borohydride: simple (1) and differential (2), combined with the hydrogen-evolution curve (3)

satisfactory solubility of calcium chloride (about 1.6 $CaCl_2$ at 20°), and the slight solubility of sodium chloride ([4]).

In the work, sodium borohydride containing 99.0% $NaBH_4$ and dehydrated calcium chloride—99.7% $CaCl_2$—were used. "Pure" grade pyridine was kept for 5-6 days over calcium hydride and then distilled over a fresh portion of hydride. Tetrahydrofuran, to remove peroxides, was treated with potassium hydroxide hydrate, then kept for 2-3 days over

metallic sodium and distilled. Calcium was determined by the complexometric method, using murexide as the indicator ([5]); the borohydride anion, by the iodate method ([6]). Special experiments showed that the presence of chemically bound THF and pyridine in the solvates does not interfere with determination of the calcium borohydride content by the iodate method.

In carrying out experiments on the synthesis of calcium borohydride according to equation (1), sodium borohydride and calcium chloride were taken in ratios of 1.5, 2, and 2.5. Sodium borohydride in the form of a 5% solution in pyridine was gradually added to a suspension of $CaCl_2$ in pyridine, contained in a three-necked flask, with continuous stirring.

Preliminary experiments showed that after 8-10 h of stirring the borohydride anion is concentrated in the solid phase, which contains, in addition, NaCl insoluble in pyridine and the residue of unreacted $CaCl_2$. The residue was then, after filtration and thorough removal of pyridine by vacuum distillation at 190°, treated with THF, in which calcium chloride and sodium chloride are practically insoluble. After distillation of THF under vacuum at room temperature, the solvate $Ca(BH_4)_2 \cdot 2THF$ crystallizes from the clear solution. Twofold recrystallization from THF makes it possible to obtain the disolvate with a purity of 99.0-99.5%.

Fig. 2. Heating curves of calcium borohydride: simple (1) and differential (2), combined with the hydrogen-evolution curve (3)

To obtain nonsolvated calcium borohydride, the disolvate was heated under vacuum for two hours with a gradual increase in temperature to +190°.

The synthesis of pure calcium borohydride can be carried out only on the basis of solubility-determination data.

Calcium borohydride in the form of the solvate $Ca(BH_4)_2 \cdot 7Py$ melts incongruently at 96°; its solubility in pyridine at 20° is 0.5 wt.% $Ca(BH_4)_2$. The solubility of calcium borohydride in THF was studied in the temperature interval −107 to

+17° by the visual-polythermal method and at +17 to +50° by the isothermal method. The solubility polytherm (Fig. 1) is characterized by the existence of two solvates, $Ca(BH_4)_2 \cdot 4THF$ and $Ca(BH_4)_2 \cdot 2THF$. The transition reaction of the tetrasolvate to the disolvate,

$$Ca(BH_4)_2 \cdot 4THF \rightleftharpoons Ca(BH_4)_2 \cdot 2THF + \text{solution}$$

corresponds to a temperature of +29° and a liquid-phase concentration of 13.8 wt.% $Ca(BH_4)_2$.

The calcium borohydride tetrasolvate $Ca(BH_4)_2 \cdot 4THF$ consists of white crystals, is unstable in air, and readily gives off part of the bound solvent, turning into the disolvate; in the presence of moisture it gradually hydrolyzes with evolution of hydrogen.

The disolvate $Ca(BH_4)_2 \cdot 2THF$ is a white, hygroscopic powder; unlike the tetrasolvate, it is completely stable in dry air and melts incongruently at +142°.

Nonsolvated calcium borohydride is a white powder with a specific gravity of 1.12 g/cm^3, stable in dry air and hygroscopic. According to data—

thermographic analysis (Fig. 2), without reaching the melting temperature, decomposes with the evolution of hydrogen. Being readily soluble in water and THF, calcium borohydride is only slightly soluble in pyridine and practically insoluble in dioxane and ether.

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Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

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