Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 3, 785–790

HYDROGEN STORAGE IN BOROHYDRIDES
Comparison of hydrolysis conditions of $LiBH_4$, $NaBH_4$ and KBH_4

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The hydrogen storage capabilities of alkaline borohydrides through a hydrolyzing process were determined by taking into consideration the hydration of the end products. Comparison of $LiBH_4$, $NaBH_4$ and KBH_4 showed their storage capacities to be dependent on the composition of the metaborate formed. This composition is ruled by the hydrolysis conditions, especially the temperature reached during the reaction and the stability of the hydrates. The borohydride with the highest hydrogen content in the solid state, $LiBH_4$, could be less efficient than KBH_4 if the hydrolysis is performed at 120°C.

Keywords: *borohydrides, hydrogen storage, hydrolysis, metaborates*

Introduction

For some years, the use of hydrogen as an energy carrier has been confronted with technical obstacles that have delayed its development. A sticking point limiting the use of hydrogen, principally for on-board applications, is its storage on board vehicles. Among the technically feasible solutions, the storage of hydrogen by regenerable chemical hydrides has been the subject of much research. Study of the gravimetric capacity of hydrogen present in chemical hydrides immediately directs attention to the alkaline or alkaline-earth borohydrides, which have a capacity higher than 18 mass% in the case of the lithium salt $LiBH_4$.

The borohydrides, or more properly the tetrahydroborates, were brought to prominence in the early fifties by Schlesinger and Brown [1] and have undergone very considerable development in organic chemistry. For several years now, these compounds have been attracting distinctly greater interest, linked to the high gravimetric percentage of hydrogen that they contain. This can be released, either by thermolysis or by controlled hydrolysis, both these methods yielding considerable mass percentages stored (Table 1).

Furthermore, some alkaline borohydrides can form aqueous or alcoholic solutions which are relatively stable over time, solutions which can be considered as a hydrogen-generating 'fuel'. The aqueous solution of stabilized sodium borohydride is particularly well adapted to on-board applications; it provides a high volumetric storage capacity and fuel supply conditions analogous to those in practice today, while meeting the safety criteria that are inseparable from use by the general public.

Hydrogen can be generated on demand, in the presence of a catalyst, in accordance with the following hydrolysis reaction [2]:

$$MBH_4+(2+n)\ H_2O \rightarrow MBO_2{\cdot}nH_2O + 4H_2$$

Considering this reaction, it is clear that half the quantity of hydrogen is derived from hydrogen contained in water. The borohydride-water combination should thus be considered as a fuel.

If the borohydrides have only been known for half a century, this is not the case of the metaborates which have been known since antiquity! Studies of the hydrolysis of the borohydrides have been reported in numerous journals surveying the possibilities for control of the generation of hydrogen [3, 4]. This

Table 1 Percentage of hydrogen present in alkaline borohydrides and released by hydrolysis

	$LiBH_4$	$NaBH_4$	KBH_4
Total hydrogen stored/mass%	18.3	10.6	7.4
Hydrogen released by hydrolysis/mass%	13.8	10.8	8.9

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1388–6150/$20.00

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point is not developed in this paper, which is more concerned with the stability of the borates and their different hydrates.

The chemical behaviour of the alkaline borohydrides is fairly variable, depending on the cation bonded to the anion BH_4^-. Lithium and magnesium salts give rise to violent hydrolyses, while sodium borohydride can lead to stable concentrated solutions when additived with base. As the simplest results were obtained using potassium borohydride, this is the cation which will be presented first in the course of the discussion.

The equilibrium diagram between the phases of the K_2O–B_2O_3–H_2O system at 30°C dates from 1906 [5] and discloses the existence of a single hydrate of potassium metaborate with the formula $KBO_2{\cdot}5/4H_2O$. The isopleth KBO_2–H_2O studied next [6] demonstrated the existence of other hydrates: $KBO_2{\cdot}4H_2O$ and $KBO_2{\cdot}1/4H_2O$, of which the domains of stability have been defined. Certain ambiguities remain as regards the composition of these hydrates, and the compounds $KBO_2{\cdot}4/3H_2O$ and $KBO_2{\cdot}1/3H_2O$ seem more probable [7]; similarly, in the ICDD crystallographic references, there are distinct differences between the diffractograms referenced.

The ternary system Na_2O–B_2O_3–H_2O, also determined at the beginning of the century [5], indicates the existence of two hydrates of sodium metaborate: the tetrahydrate $NaBO_2{\cdot}4H_2O$ and the dihydrate $NaBO_2{\cdot}2H_2O$, and the isopleth $NaBO_2$–H_2O was only similarly determined in the part rich in water on the basis of solubility measurements [4]. Nevertheless, other hydrates, $NaBO_2{\cdot}H_2O$, $NaBO_2{\cdot}1/2H_2O$ and $NaBO_2{\cdot}1/3H_2O$, have been identified without their domains of stability having been determined, and considerable differences have been observed in the X-ray diffraction diagrams of these compounds.

The ternary system Li_2O–B_2O_3–H_2O was also studied early in the century [8]. The existence of the metaborate dihydrate $LiBO_2{\cdot}2H_2O$ and the stability of the octahydrate $LiBO_2{\cdot}8H_2O$, were made clear [9]. However, the existence of the hemihydrate $LiBO_2{\cdot}1/2H_2O$ [10] seems disputed in its formulation [11–13].

A dehydration mechanism was studied more recently [14] and only the existence of the hydrates $LiBO_2{\cdot}8H_2O$ and $LiBO_2{\cdot}2H_2O$ seems certain.

The purpose of this study was to identify the domains of stability of the hydrates of lithium, sodium and potassium metaborate obtained after hydrolysis of the borohydrides $LiBH_4$, $NaBH_4$ and KBH_4, and thus to establish the experimental conditions leading to optimization of the storage yield of hydrogen.

Experimental

The hydrolysis reaction of lithium borohydride is quite rapid even at 20°C and can be relatively violent [15]. Hydrolysis of $LiBH_4$ in powder form (Acros, 95%) was carried out in a water-saturated atmosphere at ambient temperature. Much less reactive are the borohydrides of sodium and potassium, which hydrolyse slowly in aqueous solution at ambient temperature [1]. Aqueous solutions of mass concentration equal to 20 mass% were prepared from $NaBH_4$ (Acros, 98%) and KBH_4 (Aldrich, 98%) and hydrolysed by maintenance under reflux at 130°C.

The characterization by IR spectroscopy of the relative intensity of the vibration band situated at 2290 cm^{-1}, characteristic of the B–H bond, enabled the progress of the reaction to be monitored. After cooling of the solutions down to ambient temperature, the crystallized solid was dried rapidly on filter paper before characterization.

The products of the hydrolyses were identified by X-ray diffraction on powders (Panalytical X'Pert Pro) using a hermetic sample holder. This set-up engenders a slight modification of the base line of the diffractograms in the domain $15°<2\theta<26°$.

The thermogravimetric analyses (TG), were performed with a Mettler Toledo thermobalance (TGA/SDTA 851e) using silica crucibles of volume 900 μL. The differential calorimetric analyses (DCA), were performed with a Mettler Toledo calorimeter (DSC 821e) using aluminium crucibles of volume 170 μL. In both cases, the lids of the analysis crucibles were micro-perforated so that the solid and the products of gaseous decomposition are in equilibrium. The thermal and calorimetric analyses were conducted under an argon shield at a heating rate of 2°C min^{-1} in order to favour dehydration at the expense of fusion of the hydrates.

Results and discussion

The gravimetric storage capacity of hydrogen, defined as the ratio of the mass of hydrogen produced to the mass of the reagents, depends on the degree of hydration of the borate formed. In the case of sodium borohydride, $NaBH_4$, this capacity is 10.8 mass% when the anhydrous borate is produced, the reaction then being written:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$

However, this capacity drops to 7.3 mass% if the dihydrate $NaBO_2{\cdot}2H_2O$ is obtained as the last stage of the production of hydrogen and no longer reaches 5.5 mass% if the hydrolysis reaction leads to the formation of tetrahydrate $NaBO_2{\cdot}4H_2O$, according to the following equation:

$$NaBH_4 + 6H_2O \rightarrow NaBO_2{\cdot}4H_2O + 4H_2$$

It is clear that the storage performance of the borohydrides is strongly affected by the formation of metaborate hydrates and that it would be essential to control the hydrolysis conditions to optimize the storage of hydrogen.

The changes in storage capacity as a function of the hydrates formed, and hence of the initial composition of the fuel, are given in Table 2.

To determine the optimum conditions enabling the highest gravimetric yield of hydrogen, the dehydration of the product of hydrolysis of the borohydrides $LiBH_4$, $NaBH_4$ and KBH_4 was studied in order to establish the most favourable experimental conditions. It was then possible to compare the yields of hydrogen storage in the different borohydrides as a function of the hydrolysis conditions.

For reasons of simplicity, the case of the potassium salts will be presented in greater detail, and the differences in behaviour of the other metaborates will then be compared.

Characterization and stability of the products of hydrolysis of KBH_4

The main phase of the solid precipitated after hydrolysis of the solution of potassium borohydride is $KBO_2{\cdot}4/3H_2O$. The thermogravimetric curve shows three clearly distinct stages of decomposition (Fig. 1). From 30°C upwards, the water not bonded to the crystallized product is released (it represents about 5 mass%).

An X-ray diffractogram recorded on sintered powder at 80°C at a reduced pressure of $5{\cdot}10^{-2}$ mbar enables the stable hydrate to be identified as the compound $KBO_2{\cdot}4/3H_2O$ TG curve allows to determine the limits of its stability to be fixed up to a temperature of 135°C. Beyond 135°C, a mole of water is released to form the compound $KBO_2{\cdot}1/3H_2O$. Integration of the enthalpic signal enables an evaluation of the quantity of heat required for this transformation, which is 59 kJ mol^{-1}.

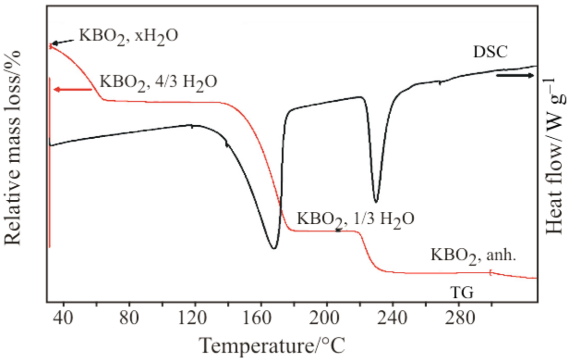

Fig. 1 TG and DSC curves of dehydration of the product of hydrolysis of KBH_4

The last hydrate breaks down from 215°C with a dehydration energy evaluated at 17 kJ mol^{-1}. The phase obtained is the anhydrous metaborate of potassium [17], confirmed by the X-ray diffraction pattern recorded on the basis of the product obtained in the thermogravimetry crucible.

It is interesting to note that the X-ray diffractograms referenced for the identification of the phases $KBO_2{\cdot}4/3H_2O$ and $KBO_2{\cdot}5/4H_2O$ are quite similar, and their differences are insufficient for identification of the products obtained after hydrolysis and dried at 80°C. Verification of the relative mass ratios between the four products distinguished by the TG removes the ambiguity regarding the degree of hydration of the borates of potassium.

Characterization and stability of the products of hydrolysis of $NaBH_4$

The solid which crystallizes at ambient temperature from the hydrolyzed solution of $NaBH_4$ is a mixture of metaborates of sodium tetrahydrate $NaBO_2{\cdot}4H_2O$ [18] and dihydrate $NaBO_2{\cdot}2H_2O$ [19].

A preliminary thermogravimetric analysis showed that tetrahydrate was highly unstable in air at ambient temperature and that it broke down into a stable hydrate up to a temperature of 80°C. The X-ray diffractogram recorded on a powder treated at 45°C enables the identification of metaborate dihydrate. In view of the very low stability of metaborate tetra-

Table 2 Changes in the potential for hydrogen storage by the borohydrides as a function of the water content of the fuel

	$LiBH_4$	$NaBH_4$	KBH_4
Molar mass of fuel with $2H_2O$/g mol^{-1}	57.8	73.8	89.9
Recoverable hydrogen/mass%	13.8	10.8	8.9
Molar mass of fuel with $4H_2O$/g mol^{-1}	93.6	109.8	125.8
Recoverable hydrogen/mass%	8.5	7.3	6.3
Molar mass of fuel with $6H_2O$/g mol^{-1}	129.8	145.8	161.9
Recoverable hydrogen/mass%	6.2	5.5	4.9

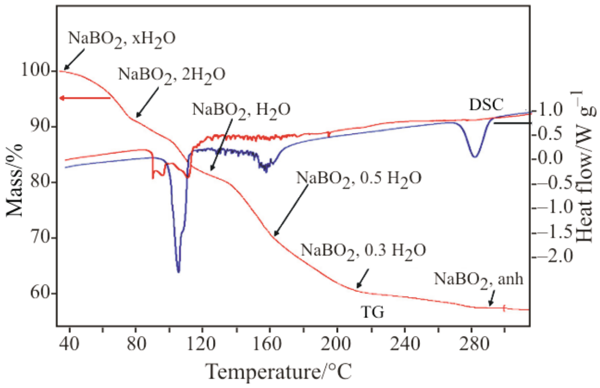

Fig. 2 TG and DSC curves recorded on the products of hydrolysis of $NaBH_4$

hydrate, the calorimetric analyses of the product of hydrolysis of the aqueous solution of $NaBH_4$ were performed on a partially dried product. The TG and DSC curves are shown in red in Fig. 2. The DSC curve obtained on commercial dihydrate has been added, in blue, to allow comparison of the DSC curves and evaluation of dehydration heat.

The presence of tetrahydrate in the product of hydrolysis is visible in the loss of mass occurring as soon as heating begins. No mass assessment is possible, however, as the low stability of tetrahydrate under the experimental conditions renders all certainty as to the initial value of its mass impossible. A plateau in the TG curve is observed up to 80°C, the temperature corresponding to the start of dehydration of the dihydrate. The derived thermogravimetric curve, DTG, not shown for clarity in the figure, enables a better definition of the different stages in dehydration to be attained. It confirms that, between 130 and 180°C, dehydration takes place in two stages. The mass loss associated with the first stage (~130–155°C) could correspond to the departure of one mole of water, whereas the mass lost observed at 155°C could be assigned to the monohydrate breakdown into hemihydrate. Quite an uncertainty remains concerning the existence of stable phases of $NaBO_2{\cdot}H_2O$ and $NaBO_2{\cdot}1/2H_2O$ since no plateau has been identifiable to characterize these phases very clearly, even using the DTG curve. Additionnally thermal treatments performed in the temperature range 130–180°C could not lead to the identification of these phases using XRD, leading us to envisage metastable phases.With heating, the loss of mass continues and attains a better defined plateau corresponding to a compound $NaBO_2{\cdot}1/3H_2O$. After this, the gradual departure of 1/3 mole of water takes place from 250°C. The hydrate $NaBO_2{\cdot}1/3H_2O$ breaks down from 250°C into an anhydrous salt, as is confirmed by the X-ray diffractogram obtained from the final product analysed [20].

The two DSC curves shown in Fig. 2 make plain the very poor crystallinity of the phases obtained by direct dehydration. The curve recorded from a commercial hydrated metaborate after prior drying at 45°C very clearly shows the thermal effects associated with dehydration: 52 kJ mol^{-1} for the change from $NaBO_2{\cdot}2H_2O$ to $NaBO_2{\cdot}H_2O$, 23 kJ mol^{-1} for the change from $NaBO_2{\cdot}H_2O$ to $NaBO_2{\cdot}1/2H_2O$ and 19 kJ mol^{-1} for the change from $NaBO_2{\cdot}1/3H_2O$ to $NaBO_2$. The change from the hydrate $NaBO_2{\cdot}H_2O$ to the hydrate $NaBO_2{\cdot}1/3H_2O$ seems to correspond, not to the actual existence of phases, but to solid solutions under the experimental conditions used. The set of values obtained leads to an average dehydration heat in the neighbourhood of 50 kJ mol^{-1} per mole of water lost by the metaborate. The second curve shown (in red) corresponds to the dried product of hydrolysis. No heat measurement is possible, as the hydrates formed are amorphous or very poorly crystallized, which does not produce usable DSC curves. Dehydration of metaborates forms highly divided products in the form of rigid foams, the structure of which prevents elimination of the water formed.

Characterization and stability of the products of hydrolysis of $LiBH_4$

The X-ray diffractogram recorded on the product of hydrolysis of $LiBH_4$ shows a well crystallized product composed of two phases identified as octahydrate of lithium metaborate $LiBO_2{\cdot}8H_2O$ [21] and dihydrate of lithium metaborate $LiBO_2{\cdot}2H_2O$ [22].

The TG curve shows that the product of the hydrolysis of $LiBH_4$ is not stable in air at ambient temperature. The mass loss (about 9%) observed up to a temperature of 57°C can be attributed to the release of 6 moles of water by the fraction of $LiBO_2{\cdot}8H_2O$ present in the solid. The plateau observed in the temperature range 57–120°C represents the domain of stability of lithium metaborate dihydrate. Identification of the dihydrate was carried out by XRD analysis of a sample heated to 85°C at a reduced pressure of $5{\cdot}10^{-2}$ mbar.

The successive stages of dehydration leading to the formation of anhydrous metaborate $LiBO_2$ are observable between 120 and 300°C, but no plateau corresponding to a definite hydrate compound is clearly visible. The overall loss of mass is about 40% with respect to the mass of $LiBO_2{\cdot}2H_2O$ (the change from dihydrate to the anhydrous compound represents a theoretical loss of 42 mass%). The product obtained after TG is very poorly crystallized and contains for the most part the anhydrous phase $LiBO_2$. The DTG curve reveals the presence of three points of inflection, centred respectively at 153, 240 and 270°C, which may be manifestations of the presence of the lower hydrates $LiBO_2·1/2H_2O$ and $LiBO_2·1/3H_2O$. These results permit the proposition that the domain of stability of dihydrate extends as far as 120°C and that of the hemihydrate $LiBO_2·1/2H_2O$ extends from 120 to 220°C. $LiBO_2·1/2H_2O$ breaks down above 220°C to form $LiBO_2·1/3H_2O$, which is stable up to 255°C.

The XRD pattern recorded on the product dried for several hours at 150°C at a reduced pressure of $5·10^{-2}$ mbar shows no X-ray diffraction lines, and strong dilatation of the product is observed during its dehydration.

The DSC curve recorded on the product of hydrolysis after prior drying at 80°C shows an endothermic peak centred at 150°C which corresponds to the first phase of dehydration of metaborate of lithium dihydrate. Dehydration continues with a low-energy and practically continuous endothermic phenomenon which comes to an end in the region of 300°C. The dehydration heat of $LiBO_2·2H_2O$ was calculated by integration of the DSC signal; it is 30 kJ mol^{-1} for the change $LiBO_2·2H_2O$ to the most stable lower hydrate $LiBO_2·1/2H_2O$, i.e. about 20 kJ mol^{-1} of water loss.

Conclusions

The results presented in this paper concern the stability of metaborate hydrates produced by the hydrolysis of borohydrides. Strictly identical dehydration operating conditions (heating rate of 2°C min^{-1} at atmospheric pressure) were adopted for the three alkaline metaborates.

Study of the thermogravimetric analysis curves determined the hydrates taken into consideration for each of the metaborates, and their domains of stability:

- for potassium metaborate: $KBO_2·4/3H_2O$ stable up to 135°C and $KBO_2·1/3H_2O$ stable from 135 to 215°C.
- for sodium metaborate: $NaBO_2·2H_2O$ stable up to 80°C, $NaBO_2·H_2O$ and $NaBO_2·1/2H_2O$ metastable phases appearing in the temperature range 80–180°C and $NaBO_2·1/3H_2O$ stable from 180 to 230°C.
- for lithium metaborate: $LiBO_2·2H_2O$ stable from ambient temperature up to 120°C, $LiBO_2·1/2H_2O$ stable from 120 to 220°C and $LiBO_2·1/3H_2O$ stable up to 255°C.

Figure 3 shows the results obtained for each borohydride as a function of the temperature at which the end of hydrolysis took place.

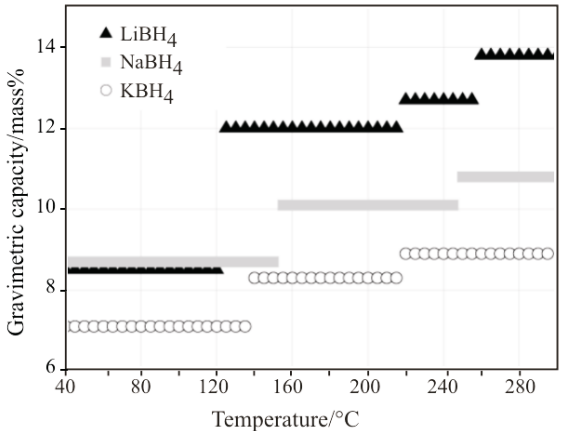

Fig. 3 Comparison of the hydrogen storage capacities of different alkaline borohydrides

The experimental results enable comparisons to be made between the hydrogen gravimetric storage capacities of the three borohydrides as a function of the hydration rates of the borate formed and the temperature of hydrolysis.

Although lithium borohydride possesses the highest mass percentage of hydrogen among the alkaline borohydrides, its use when a mode of hydrogen release by hydrolysis is employed should not lead to performance much superior to that of the other alkaline borohydrides. This is due to the greater stability of the hydrates of the lithium metaborates, which retain a considerable proportion of the water involved during hydrolysis. Sodium borohydride, although it displays a lower mass percentage, has shown itself capable of better storage performance up to hydrolysis temperatures of 120°C. Hydrogen gravimetric storage capacities of nearly 8.5% were easily obtained, values superior to the majority of the systems currently under development. The fuel that generates the hydrogen is composed of a mixture of water and sodium borohydride, it presents no danger to the environment and should achieve significant and rapid industrial development.

If the hydrolysis temperature is of the order of 150°C, a value easily attained in view of the very great exothermicity of the hydrolysis reaction, storage of 10 mass% may be obtained, a value that has currently been retained as the objective to be achieved by 2015 for the development of hydrogen as an energy carrier. The storage of hydrogen using borohydrides and a mechanism for the production of hydrogen by controlled hydrolysis can constitute a solution offering considerable advantages.

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Received: February 25, 2008
Accepted: August 27, 2008

DOI: 10.1007/s10973-008-9073-4