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Abstract

Ammonia borane NH_3BH_3 is able to generate H_2 by catalytic hydrolysis at ambient conditions. Such a potential has been much studied but the hydrolysis by-products, i.e. ammonium borates, have been little studied. As such we undertook a systematic work aiming at getting a sound understanding of the borates forming by hydrolysis. Contrary to what is commonly believed, NH_3BH_3 (10 M) in aqueous alkaline (pH = 8) solution is not completely stable. Spontaneous hydrolysis takes place, resulting in the formation of by-products and precipitation of *borate crystals*. This means that long-term storage of concentrated AB solution is not possible. The *borate crystals* were analyzed with the help of various techniques and was identified as being diammonium tetraborate dihydrate $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ (263.39 g mol^{-1}). The crystal structure was solved and found to be monoclinic with a space group $P2_1$. The borate is an analog of borax $Na_2B_4O_5(OH)_4{\cdot}8H_2O$. These results, among others, are reported in details hereafter and they are discussed in order to bring elements of response to the questions concerning storage of aqueous NH_3BH_3 and recyclability of such a borate.

Keywords

Ammonia borane; Borate; Hydrogen storage; Hydrolysis; Polyborate; Tetraborate.

1. Introduction

Ammonia borane NH_3BH_3 (AB) is a prominent boron-based material in the field of chemical hydrogen storage. Though known since the middle of the last century [1], the interest in it, for the mentioned application, started in the mid-2010s, especially as a result of two pioneering works. On the one hand, Gutowska et al. [2] demonstrated that the dehydrogenation properties of AB under heating are substantially improved when a nanoscaffold (e.g. mesoporous silica) is used to destabilize it. On the other hand, Chandra and Xu [3] showed that rapid dehydrogenation of AB is feasible, at ambient conditions, by dissociation and catalytic hydrolysis. Since then, dehydrogenation of AB by thermolysis or hydrolysis has been widely investigated, each of these approaches having their own advantages and drawbacks [4-6].

Before AB, another boron-based material, namely sodium borohydride $NaBH_4$, showed interesting dehydrogenation properties by hydrolysis [7]. AB was suggested to be a good alternative mainly because $NaBH_4$ is not stable in aqueous solution [8]. For example, Chandra and Xu [9] reported that a slightly concentrated (0.1 M) solution of AB (pH of 9.1) kept under argon atmosphere is fairly stable and, above all, much more stable than a $NaBH_4$ solution. Hence, hydrolysis of AB requires a catalyst to generate H_2 with fast kinetics [3], which has given rise to great efforts in developing a lot of active catalysts [10-13]. In contrast, other aspects related to the hydrolysis reaction (e.g. effective storage capacity maximization, H_2 purity, reaction intermediates analysis, by-products identification) have been far less explored [5,6].

The basic argument against hydrolysis of $NaBH_4$ is that sodium tetrahydroxyborate $NaB(OH)_4$, the reaction by-product, is awkwardly transformed (i.e. reduced) back into $NaBH_4$ [14]. Simply put, the B–O bond in the anion $B(OH)_4^-$ is, roughly, as stable as the C–O bond in CO_2 [15], both compounds facing thus comparable conversion challenges. This also applies to AB in hydrolysis, and yet, little is known about its by-products.

Chandra and Xu [3,9] reported, without further discussion, the formation of boric acid $B(OH)_3$ and of the metaborate anion BO_2^-, as well as the formation of other borates that coexist in solution via pH-dependent equilibria:

$$NH_3BH_3\ (aq) + 2H_2O\ (l) \rightarrow NH_4^+\ (aq) + BO_2^-\ (aq) + 3H_2\ (g) \qquad (1)$$

NH_3BH_3 (aq) + $3H_2O$ (l) → NH_3 (aq) + $B(OH)_3$ (aq) + $3H_2$ (g) (2)

Mohajeri et al. [16] corroborated and, added that the by-product in solid state was crystallized $B(OH)_3$. Using in situ ^{11}B NMR, Liu et al. [17] concluded that the formation of aqueous $B(OH)_3$ (Eq. 2) took place, whereas Rachiero et al. [18,19], stressed on the formation of aqueous $B(OH)_4^-$:

NH_3BH_3 (aq) + $4H_2O$ (l) → NH_4^+ (aq) + $B(OH)_4^-$ (aq) + $3H_2$ (g) (3)

Both species, i.e. $B(OH)_3$ and $B(OH)_4^-$, are likely to form and their formation is mainly pH-dependent (pKa of $B(OH)_3/B(OH)_4^-$ equal to 9.1). Rachiero et al. [18,19] and Hannauer et al. [20] suggested reactions between the $B(OH)_3$ and $B(OH)_4^-$ entities, resulting in equilibria with polyborate species like $B_3O_3(OH)_4^-$. The following path was notably suggested:

$2B(OH)_3$ (aq) + $B(OH)_4^-$ (aq) ↔ $B_3O_3(OH)_4^-$ (aq) + $3H_2O$ (l) (4)

For the solid recovered after water extraction, they identified, by pattern matching, ammonium tetraborate tetrahydrate $(NH_4)_2B_4O_7{\cdot}4H_2O$. Ramachandran and Gagare [21] studied a concentrated AB solution (10.8 M). A crystallized borate salt was recovered and, by X-ray crystallography, its structure was determined, at 50% probability, as ammonium tetraborate hydrate $(NH_4)_2B_4O_5(OH)_4{\cdot}1.4H_2O$. Moussa et al. [22] prepared a set of borates by extraction of water at different temperatures (–50, 0, 80, 120, 200 and 300°C). A series of ammonium pentaborates (e.g. $NH_4B_5O_6(OH)_4{\cdot}2H_2O$ and $NH_4B_5O_6(OH)_4$) were suggested together with $B(OH)_3$, HBO_2 and B_2O_3 (depending on the temperature). Chou et al. [23] focused on incomplete hydrolysis of AB, which was performed by using a limited amount of water (less than the stoichiometry in Eq. 3). Mixtures of $B(OH)_3$ and metaboric acid HBO_2 were found to be the dominant products in such conditions.

It is important to have a sound understanding of the borates forming by hydrolysis of AB. Borates form, but their nature depends on a number of experimental factors (AB concentration, solution pH, water amount, atmosphere, water extraction and drying processes). On another note, AB is not so stable in aqueous alkaline solution. For example, a careful analysis of the ^{11}B NMR data reported by Chandra and Xu [3,9] shows at least one additional signal at a positive chemical shifts, which was due to a borate species. Hence, we initiated a new study aiming at recovering and analyzing crystallized borates forming by spontaneous hydrolysis of AB (10 M). We isolated

crystals of diammonium tetraborate dihydrate $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ (263.39 g mol^{-1}). This compound is a less-hydrated ammonium analog of borax $Na_2B_4O_5(OH)_4{\cdot}8H_2O$ (disodium tetraborate octahydrate). Our results are described hereafter and discussed to bring elements of response to the questions concerning storage of AB in aqueous solution.

2. Experimental

Ammonia borane NH_3BH_3 (borane-ammonia complex; CAS number 13774-81-7; 97% from Merck) was stored in an argon-filled glove box (MBraun M200B; O_2 and H_2O < 0.1 ppm). Sodium hydroxide NaOH (CAS number 1310-73-2; from Alfa Aesar) was also used as received. With respect to deionized ultra-pure water (Milli-Q grade, resistivity > 18 MΩ cm), it was systematically bubbled with argon just after extraction from our purification system, and it was used to prepare an alkaline solution (pH adjusted at 8) under argon flux. All of the solutions were in fact kept under argon atmosphere to avoid dissolution of carbon dioxide CO_2 from air and subsequent formation of carbonic acid H_2CO_3:

$$H_2O\ (l) + CO_2\ (g) \leftrightarrow H_2CO_3\ (aq) \quad (5a)$$

$$H_2CO_3\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + HCO_3^-\ (aq) \quad (5b)$$

The NH_3BH_3 solution (10 M) was prepared as follows. In the glove box, 308 mg of NH_3BH_3 was weighted and transferred in a vial which was sealed with a septum. Under argon, 1 mL of the aqueous alkaline solution was injected through the septum. After complete dissolution of NH_3BH_3, the sealed vial, under an argon atmosphere, was put in a heat chamber initially at 35 °C (dark conditions). The temperature of the chamber was decreased by 1 °C every week. Degassing (to evacuate the generated H_2) was performed when the septum got curved, which was done by briefly puncturing the septum. Crystals were visible when the temperature dropped below 25 °C. They were extracted from the solution and transferred in a clean vial (in the glove box). They were put under vacuum overnight and finally stored under argon atmosphere.

The crystals were visualized using a digital microscope (Keyence VHX-6000) and, analyzed by different techniques: Fourier transform infrared (FTIR) spectroscopy (FTIR; IS50 Thermo Fisher Scientific); Raman spectroscopy (Horiba Jobin Yvon LabRAM 1B; laser Ar/Kr 100 mW 647.1

nm); X-ray photoelectron spectroscopy (XPS; ESCALAB 250 from Thermo Electron; monochromatic source Al Kα ray 1486.6 eV; analyzed surface of 400 µm diameter; binding energies (BE) of all core levels referred to the C–C of C1s carbon at 284.8 eV); thermogravimetric (TG) analysis (Netzsch STA 449 F1 Jupiter) coupled to mass spectrometry (MS; Netzsch QMS 403D Aëolos Quadro) for gas analysis; and, differential scanning calorimetry (DSC; DSC; Q600, TA Instruments). ^{11}B nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCE-300; probe head BBO10, 96.29 MHz, D_2O in a capillary tube) was used to analyze the solutions obtained by dissolution of the crystals in deionized water and methanol (CAS number 67-56-1; ≥99.9% from Merck).

Part of the as-obtained single crystal was analyzed by X-ray diffraction. X-ray single-crystal structural data were collected on a Bruker D8 VENTURE equipped with a PHOTON II CPAD detector and a microfocus X-ray source with Cu-K_α radiation (λ = 1.54184 Å) operating at 50 kV and 1 mA. A suitable crystal was chosen and mounted on a 150 µm aperture Dual-Thickness Microloop. The data collection was performed at −173 °C and at ambient temperature. The as-obtained unit cell and space group showed that the structures were identical. We therefore decided to report the data collected at −173 °C. The single crystal X-ray diffraction allowed collecting a total of 1496 frames. The total exposure time was 8.31 h. The frames were integrated with the Bruker SAINT Software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 4196 reflections to a maximum θ angle of 55.06° (resolution of 0.94 Å). The final cell constants (as reported hereafter, in sub-section 3.4) are based upon the refinement of the XYZ-centroids of 3948 reflections above 20 σ(I) with $12.38° < 2\theta < 110.1°$. The data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.797. The space group was determined using XPREP implemented in APEX3. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2014 (full-matrix least-squares on F^2) contained in WinGX. The crystal data, refinement conditions and crystal structure are reported hereafter, in sub-section 3.4.

3. Results

3.1. Preliminary observation

Crystallization (and precipitation) of pure AB generally results in needle-like forms [24]. In our conditions, bulky and shaped crystals were recovered. An example is shown in Figure 1. The crystal looks very similar to crystals of ammonium pentaborate $(NH_4)_2O{\cdot}5B_2O_3{\cdot}8H_2O$ [25]. From this observation, evolution of AB into a borate, by hydrolysis, was assumed to take place. Hereafter, the as-formed solid will be called *borate crystal*.

Figure 1. Digital microscope observation of one of our millimeter-scale *borate crystals* recovered after hydrolysis of AB in alkaline conditions: magnification ×100; angle of rotation 0°; scale bar 100 µm.

3.2. Analysis by spectroscopy

The formation of a borate was first verified by ^{11}B NMR spectroscopy. Fragments of the *borate crystal* were solubilized in two different solvents, namely water and methanol (Figure 2). With the former solvent, a singlet peaking at +16.2 ppm is noticed; it is typical of a borate [26]. With methanol as solvent, there are two overlapping singlets peaking at +18.8 and +17 ppm. It is likely that some –OH groups of the borate were substituted by $–OCH_3$ groups.

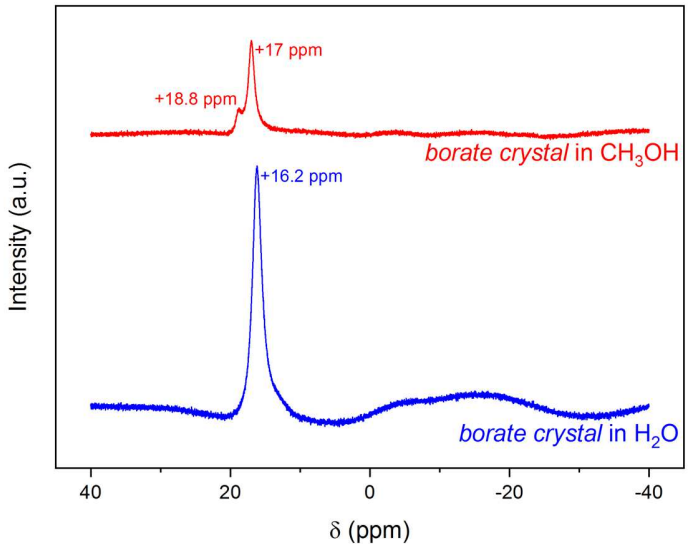

Figure 2. ^{11}B NMR spectra of the *borate crystal* in water and in methanol.

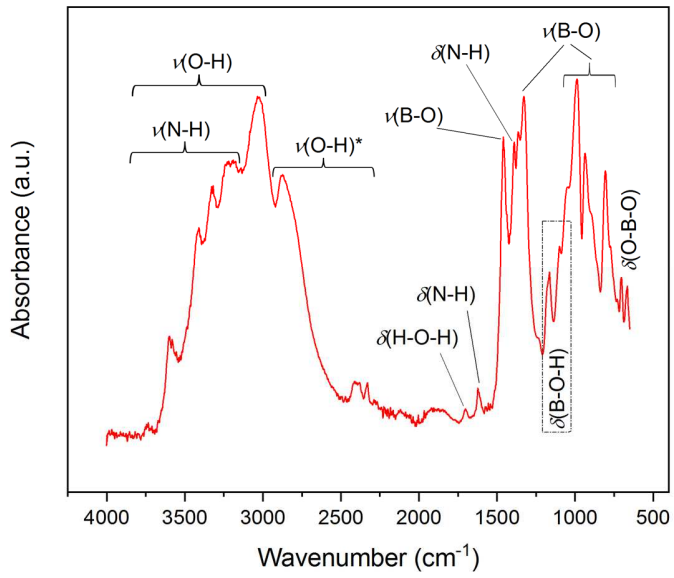

Figure 3. FTIR spectrum of the *borate crystal* (* for O–H bonds involved in hydrogen bonding).

The FTIR fingerprint of the *borate crystal* (Figure 3) is comparable to that of di-, tetra- and penta-borates [27]. Stretching and deformation modes for B–O, O–H (including O–H involved in hydrogen bonding), B–O–H, and N–H bonds can be seen. They confirm the transformation of AB into a borate species.

Similar observations can be made for the Raman spectrum (Figure 4). Otherwise, there is an intense band at 583 cm^{-1} due to B–O bonds. Interestingly, it matches the band due to B–O bonds found in the anion $B_4O_5(OH)_4^{2-}$ [28,29], and specifically in borax $Na_2B_4O_5(OH)_4{\cdot}8H_2O$ [30].

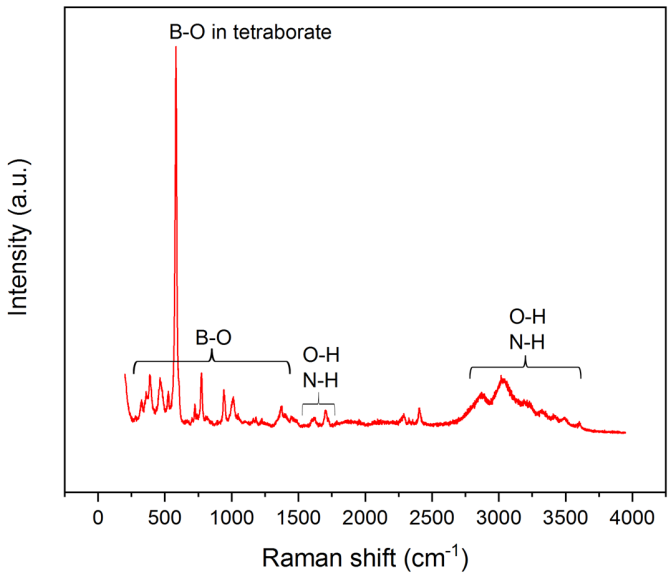

Figure 4. Raman spectrum of the *borate crystal*.

The *borate crystal* was analyzed by XPS (Figure 5). Besides the C element, the survey scan shows the presence of B, N and O. The binding energy of B (1s) is 192.7 eV, which is typical of a boron oxide. According to the NIST database [31], the energy 192.7 eV (± 0.1 eV) is typical of e.g. boric acid $B(OH)_3$, boron oxide B_2O_3, the tetraborate anion $B_4O_7^{2-}$, ammonium tetraborate tetrahydrate $(NH_4)_2B_4O_7{\cdot}4H_2O$, and also $(NH_4)_2O{\cdot}5B_2O_3{\cdot}8H_2O$. The binding energy of O (1s) is 532.5 eV and is comparable to that of e.g. B_2O_3. The binding energy of N (1s) is 401.9 eV, a

value found for a number of ammonium salts. It may be concluded that the XPS data suggest the formation of an ammonium (poly)borate.

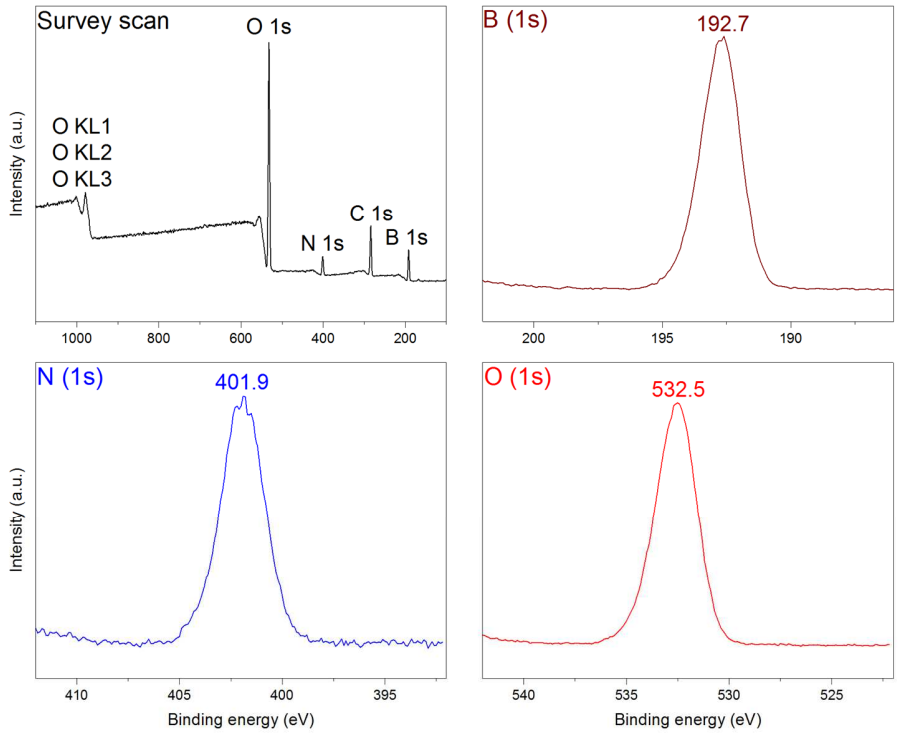

Figure 5. XPS spectra of the *borate crystal*: i.e. survey scan, and focuses on B (1s), N (1s) and O (1s).

3.3. Thermal and calorimetric analysis

The thermal behavior of the *borate crystal* was studied by TG analysis and DSC (Figure 6). The released gases were analyzed by MS (Figure 6) and the following *m/z* values were collected (in order of the signals intensity): 17, 18, 16 and 15. The intensity of the signal *m/z* = 18 is comparable to that of the signal *m/z* = 17. For pure H_2O, the relative intensity between these two signals should have been 5:1. In our conditions, the relative intensity is close to 1. Our results thus indicate that H_2O (with *m/z* = 18, 17 and 16) formed by dehydration and NH_3 (with *m/z* = 17, 16 and 15) formed by deammoniation. Similar observations are reported elsewhere, for the thermal decomposition of $(NH_4)_2O{\cdot}5B_2O_3{\cdot}8H_2O$ [25].

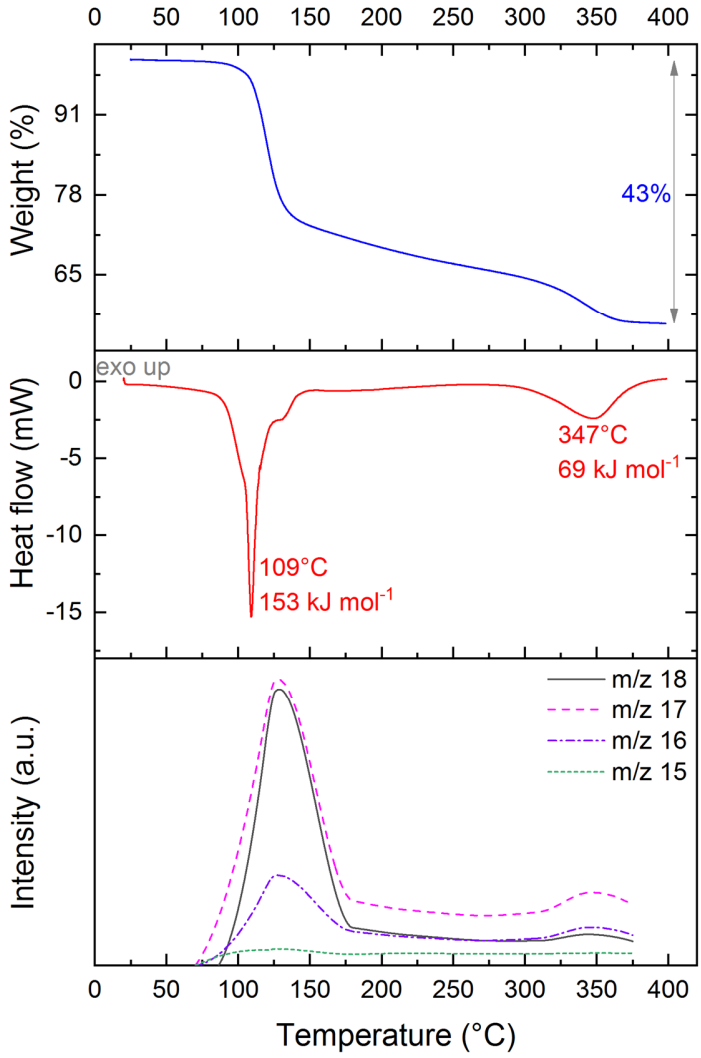

Figure 6. TG analysis, DSC and MS results for the *borate crystal* (heating rate 5 °C min^{-1}).

The thermal decomposition of the *borate crystal* is stepwise, showing two main weight losses. From 75 to 250 °C, the *borate crystal* overcomes a significant loss of H_2O and NH_3 (33.2% in weight); the process is featured by an endothermic signal (153 kJ mol^{-1}) peaking at 109 °C. A roughly comparable energy (187 kJ mol^{-1}) was reported for dehydration (3 H_2O out of 8) of $(NH_4)_2O{\cdot}5B_2O_3{\cdot}8H_2O$, the process peaking at higher temperature (175 °C) [25]. Above 250 °C and up to 400 °C, the *borate crystal* continues to decompose. The weight loss is less important (9.8%). This event is featured by an endothermic signal (69 kJ mol^{-1}) peaking at 347 °C. A

similar energy (67 kJ mol^{-1}) was reported for $(NH_4)_2O{\cdot}5B_2O_3{\cdot}5H_2O$; this polyborate liberated 2 equiv H_2O in a process peaking at 311 °C [25].

Our TG and DSC curves were compared to curves obtained with a compound reported to be ammonium tetraborate tetrahydrate (263.2 g mol^{-1}) [32]. Unfortunately, there is no detail about its preparation or origins. From the information that can be found on the internet (especially from suppliers of chemicals), this compound would be $(NH_4)_2B_4O_7{\cdot}4H_2O$ (Figure 7). The comparison shows similarities (Table 1): above 75 °C the TG results are similar; the endothermic signals peak at similar temperatures; there is the co-release of H_2O and NH_3 over the range 75-400 °C. The comparison also shows one key difference: with $(NH_4)_2B_4O_7{\cdot}4H_2O$, there is a preliminary weight loss, below 75 °C, due to the release of 1 equiv H_2O (release of crystal water), which is associated to an endothermic signal peaking at 59 °C. In terms of weight loss measured at 400 °C, the values are roughly comparable: the loss is 43% for the present borate and it is 40.2% for $(NH_4)_2B_4O_7{\cdot}4H_2O$ (if the dehydration process occurring below 75 °C is not taken into account). From these observations, it is reasonable to conclude that the borate reported herein and the $(NH_4)_2B_4O_7{\cdot}4H_2O$ reported elsewhere looks similar, even though our borate has structure water only.

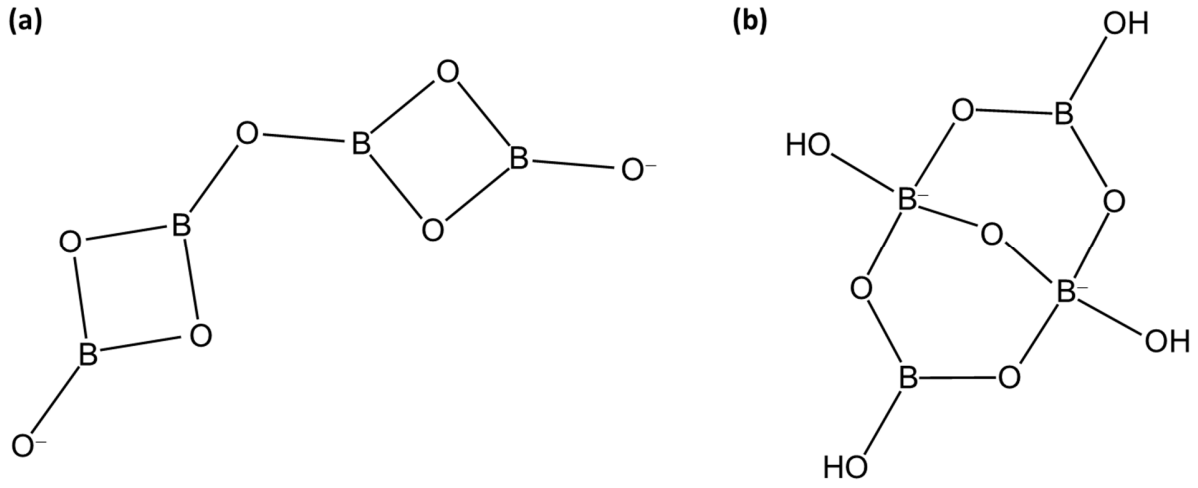

Figure 7. (a) $B_4O_7^{2-}$ anion of $(NH_4)_2B_4O_7{\cdot}4H_2O$ in ref. [32]. (b) $B_4O_5(OH)_4^{2-}$ anion of $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ of the present work and of the borax mineral $Na_2B_4O_5(OH)_4{\cdot}10H_2O$.

Table 1. Comparison of the present *borate crystal* to $(NH_4)_2B_4O_7{\cdot}4H_2O$ in reference [32], in terms of TG analysis, DSC and MS results.

Temperature range (°C)		**The *borate crystal*** *present work*	**$(NH_4)_2B_4O_7{\cdot}4H_2O$** *in ref.* [32]
20-75	Weight loss (%) by TG analysis	0	6.9
	DSC peak temperature (°C)		59
	Evolving gases by MS		H_2O
75-250	Weight loss (%) by TG analysis	33.2	28.2
	DSC peak temperature (°C)	109	110
	Evolving gases by MS	H_2O and NH_3	H_2O and NH_3
251-400	Weight loss (%) by TG analysis	9.8	12
	DSC peak temperature (°C)	347	335
	Evolving gases by MS	H_2O and NH_3	H_2O and NH_3
20-400	Weight loss by TG analysis	43	47.1

3.4. Structural analysis

A portion of the *borate crystal* was analyzed by single crystal X-ray diffraction. The crystal data and the refinement conditions are shown in Table 2. In good agreement with the results reported above, the *borate crystal* was identified to be an ammonium polyborate salt of formulae $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ (diammonium tetraborate dihydrate; 263.39 g mol^{-1}). The crystal system is monoclinic, and the space group is $P2_1$. The cell constants were found to be such as: a = 7.15996(6) Å, b = 10.6344(9) Å, c = 7.2331(6) Å, β = 98.593(3)°, V = 544.55(5) $Å^3$. The crystal structure is shown in Figure 8.

Diammonium tetraborate dihydrate is structured around the anion $B_4O_5(OH)_4^{2-}$ (Figure 9), as is the case for borax [33]. They both crystallize in monoclinic system, but they have different space groups ($P2_1$ and $C2/c$ respectively). Diammonium tetraborate dihydrate is comparable to the compound reported by Ramachandran and Gagare [21]. They suggested the formulae $(NH_4)_2B_4O_5(OH)_4{\cdot}1.4H_2O$, which was crystallographically determined at 50% probability. Our $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ and the $(NH_4)_2B_4O_5(OH)_4{\cdot}1.4H_2O$ are isostructural (monoclinic, s.g. $P2_1$). The cell constants of $(NH_4)_2B_4O_5(OH)_4{\cdot}1.4H_2O$ were calculated as being as follows: a = 7.1997(8) Å, b = 10.6039(6) Å, c = 7.2604(8) Å, β = 98.537(6)°, V = 548.153 $Å^3$.

Table 2. Space group, unit cell parameters, goodness of fit (GoF), R values, and structural parameters for the refined structure of the *borate crystal* identified to be $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$.

Empirical formula		$(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ $B_4H_{16}N_2O_{11}$
Formula weight (g mol^{-1})		263.39
Temperature (°C)		–173
Wavelength (Å)		1.54178
Crystal system, space group		Monoclinic, $P2_1$
Unit cell dimensions	a (Å)	7.15996(6)
	b (Å)	10.6344(9)
	c (Å)	7.2331(6)
	β (°)	98.593(3)
Cell volume (Å^3)		544.55(8)
Z		2
Calculated density (g cm^{-3})		1.606
Absorption coefficient (mm^{-1})		1.42
F(000)		276
Crystal size (mm)		0.02 × 0.03 × 0.03
θ range for data collection (°)		6.2–68.3
Limiting indices		$-8 \le h \le 8$, $-12 \le k \le 12$, $-8 \le l \le 8$
Completeness to θ = 68.3°		99.7%
Refinement method		Full-matrix least-squares on F^2
Data / restraints / parameters		1989 / 14 /191
Goodness-of-fit on F^2		1.14
Final R indices [$I > 2\sigma(I)$]		0.036 and 0.039
R indices (all data)		0105 and 0.114
Largest diff. peak and hole (e Å^{-3})		0.50 and -0.56

4. Discussion

In our conditions, the concentrated solution of AB (10 M) evolved towards formation and precipitation of diammonium tetraborate dihydrate $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$. For diluted solutions of AB, the main products are generally $B(OH)_3$ and $B(OH)_4^-$. Depending on the experimental conditions, especially the pH, these two species were suggested to coexist [3,9,16] or preferentially form (the one at the expense of the other) [17-19]. Nevertheless, some

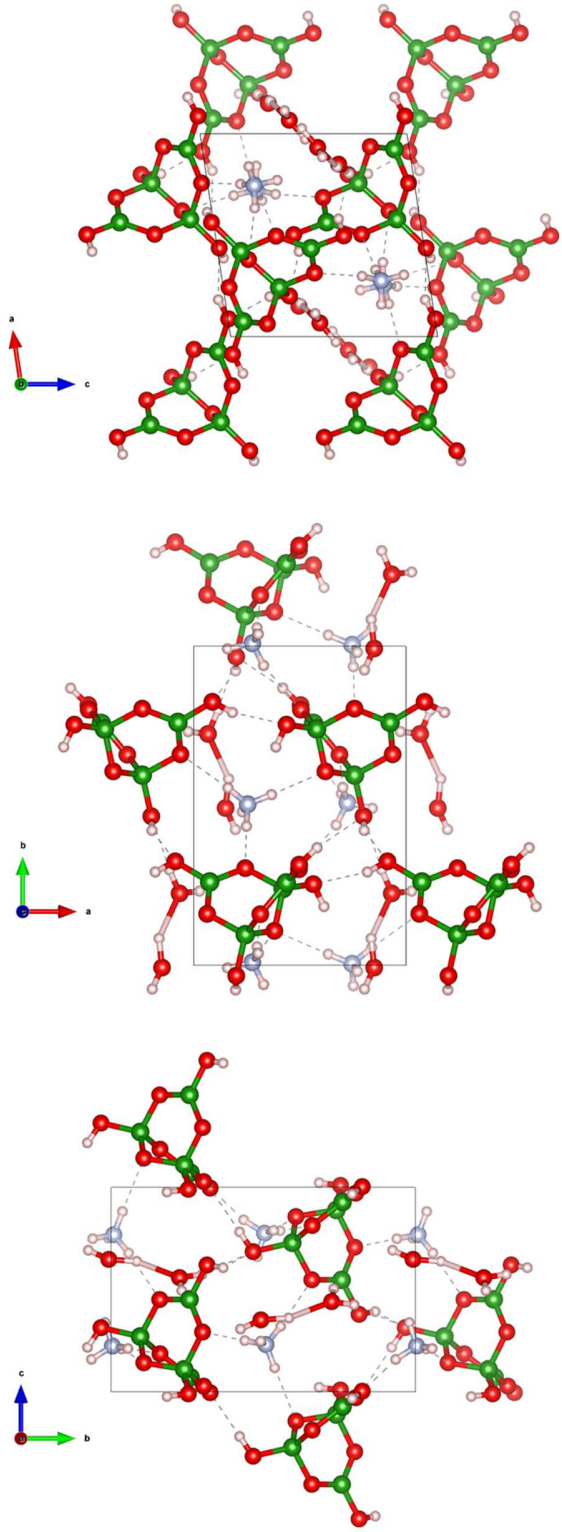

Figure 8. Crystal structure of the *borate crystal* $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ along the a, b and c crystallographic axes. The pink, green, red and blue spheres correspond to the H, B, O and N atoms respectively.

form of consensus exists on the fact that, after the hydrolysis reaction, $B(OH)_3$ and $B(OH)_4^-$ interact, polyborates form, and equilibria between all of these species take place [3,9,16-19,22]. In fact, this is a well-documented property of $B(OH)_3$ and $B(OH)_4^-$. For instance, Spessard [34] and Mesmer et al. [35] in the 1970s, and more recently Zhou et al. [36], investigated such equilibria in different conditions (pH, in the presence of neutral salt, at elevated temperature). It was established that there is an equilibrium leading to the anion $B_4O_5(OH)_4^{2-}$ (Eq. 6b), which may explain the precipitation of $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ in our experimental conditions:

$$4NH_3BH_3\ (aq) + 14H_2O\ (l) \rightarrow 2NH_3\ (aq) + 2NH_4^+\ (aq) + 2B(OH)_3\ (aq) + 2B(OH)_4^-\ (aq) + 12H_2\ (g) \quad (6a)$$

$$2B(OH)_3\ (aq) + 2B(OH)_4^-\ (aq) \leftrightarrow B_4O_5(OH)_4^{2-}\ (aq) + 5H_2O\ (l) \quad (6b)$$

$$2NH_4^+\ (aq) + B_4O_5(OH)_4^{2-}\ (aq) + 2H_2O\ (l) \rightarrow (NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O\ (s) \quad (6c)$$

The balanced chemical equation is then:

$$4NH_3BH_3\ (aq) + 11H_2O\ (l) \rightarrow + 12H_2\ (g) + 2NH_3\ (aq) + (NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O\ (s) \quad (6d)$$

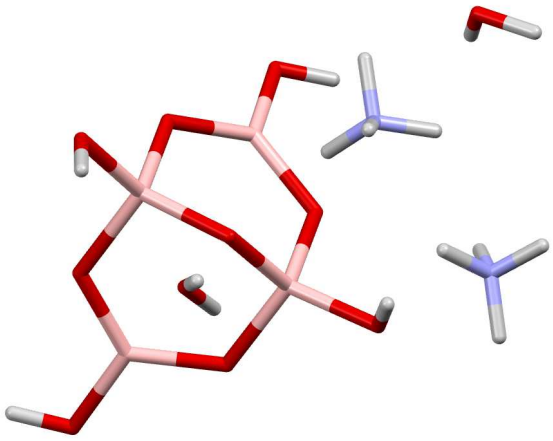

Figure 9. The $B_4O_5(OH)_4^{2-}$ anion of the diammonium tetraborate dihydrate, consistently with the molecular structure shown in Figure 7b. The NH_4^+ cations and the two H_2O molecules are also shown.

It is of interest to discuss the two "free" NH_3 molecules shown in Eq. 6d. They can pass in the gas phase, being then liberated together with H_2 generated by hydrolysis, as reported elsewhere [17,21,37]. This causes problems. The first one is related to the pollution of the H_2 stream [38]. Purification is then required which is detrimental to the cost of the technology. The second problem can be discussed in terms of "green chemistry" [39]. Loss of the aforementioned NH_3

molecules runs counter to the “green chemistry” principles like the following ones: “prevent waste”, “maximize atom economy”, “design chemicals and products to degrade after use”.

As briefly mentioned in the introduction, sodium borohydride in hydrolytic conditions has been criticized because of its instability in water at any pH [8]. AB was then presented as a stable alternative and it has been widely investigated. However, AB also evolves, spontaneously, in aqueous alkaline solution (i.e. in the absence of a catalyst). In our conditions, the AB concentration is high (10 M), which is realistic from the point of the view of a possible technological application. In such conditions, crystals of $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ precipitate after some days. In other words, AB in hydrolytic conditions should encounter the same problems as sodium borohydride [40], namely, difficult long-term storage of concentrated AB solutions because of evolution by hydrolysis, safety issues because of uncontrolled generation of H_2, and plugging of storage system pipes due to precipitation of borate crystals.

Little efforts have been focused on the identification of the condition-dependent borate products and, in conjunction with this, on the development of AB-dedicated recycling and regeneration approaches [5,6]. Here, we have shown the precipitation of $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$. It is an analog of borax $Na_2B_4O_5(OH)_4{\cdot}2H_2O$. Borax is the boron source in the process leading to the production of $NaBH_4$ via the so-called Brown-Schlesinger process: i.e. acidic attack (H_2SO_4) of $Na_2B_4O_5(OH)_4{\cdot}2H_2O$ to form $B(OH)_3$; reaction of $B(OH)_3$ with methanol resulting in $B(OCH_3)_3$; and, reduction of $B(OCH_3)_3$ by NaH to get $NaBH_4$ [41]. The present $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ could be directly used to be transformed into $NaBH_4$ by slightly adapting the aforementioned process. Otherwise, the NMR results presented above have shown transformation of $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ by reaction with methanol. One may assume that $B(OCH_3)_3$ formed. Further works are required to clear up this point; for instance, such $B(OCH_3)_3$ might be the key compound of a modified version of the aforementioned Brown-Schlesinger process.

5. Conclusion

In the present work, we considered an aqueous alkaline solution of concentrated AB (10 M). Spontaneous hydrolysis of AB took place, resulting in generation of H_2 and, formation and precipitation of *borate crystals*. Aqueous AB is thus not stable, in our conditions, and long-term storage of such a fuel appears to be difficult. The *borate crystals* were isolated to be analyzed by various techniques, and the collected data indicated the formation of diammonium tetraborate dihydrate $(NH_4)_2B_4O_5(OH)_4{\cdot}2H_2O$ (263.39 g mol^{-1}), an ammonium analog of borax $Na_2B_4O_5(OH)_4{\cdot}8H_2O$. The crystal structure was solved and was found to be as follows: monoclinic, space group $P2_1$, Z = 2, a = 7.15996(6) Å, b = 10.6344(9) Å, c = 7.2331(6) Å, β = 98.704(3) °, V = 544.5(5) $Å^3$. Diammonium tetraborate dihydrate is a new borate. It was not known as a possible borate forming by hydrolysis of AB. Henceforth, it contributes to expanding the list of the possible borate by-products coming from AB.

In hydrolytic conditions, AB can be compared to $NaBH_4$. The present work has shown that both encounter the same problems, namely difficult long-term storage of their aqueous alkaline solutions, safety issues due to uncontrolled H_2 generation, and precipitation of borates. In fact, AB in hydrolytic conditions encounters another problem. More than one borate seems to form, depending on the hydrolysis conditions. This is an issue from the recycling point of view. Further works are required to clear up this point, mainly because the industrial future of AB, if any, will be entirely dependent on its regeneration from its various borate by-products.

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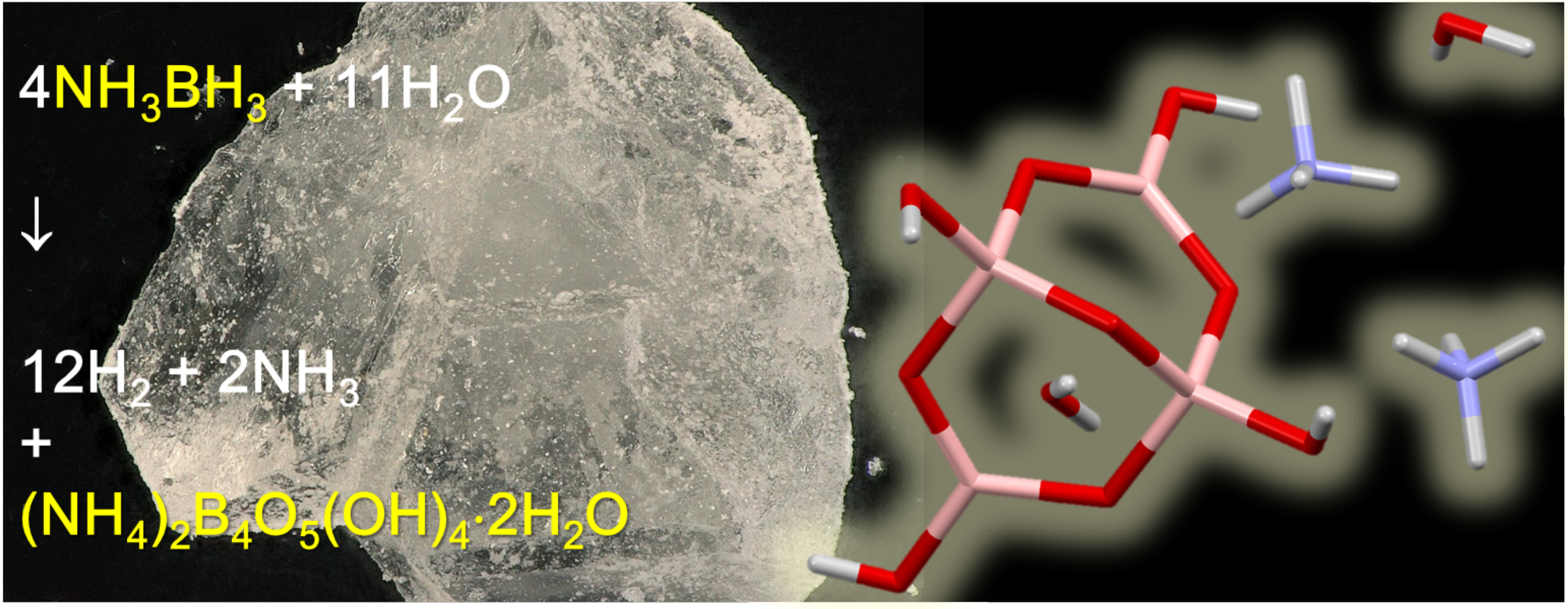
$4NH_3BH_3 + 11H_2O$
↓
$12H_2 + 2NH_3$
+
$(NH_4)_2B_4O_5(OH)_4 \cdot 2H_2O$