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Heat Effects of the Thermal Decomposition of Amidoboranes of Potassium, Calcium, and Strontium

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Abstract—Thermal effects of the decomposition of potassium, calcium, and strontium amidoboranes at 354, 421, and 483 K are determined via drop calorimetry. The processes of decomposition are weakly exothermic and accompanied by the evolution of hydrogen. Upon the decomposition of calcium amidoborane at 421 K, a prolonged exothermic process is first observed; it is then followed by an endothermic effect, due possibly to the slow structural rearrangement of the product of decomposition. The solid products of decomposition are characterized by solid-state ^{11}B NMR, FTIR spectroscopy, and mass spectrometry.

Keywords: drop calorimetry, amidoboranes, potassium, calcium, strontium

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INTRODUCTION

Amidoboranes of alkali and alkaline-earth metals are considered promising solid-phase hydrogen carriers for hydrogen energy [1−3]. Their thermal decomposition with the evolution of molecular hydrogen begins around 330 K and proceeds in two stages [4]. The evolved hydrogen contains no undesirable borazine [5, 6]; according to [6], however, it is contaminated with ammonia. According to data from TGA and DSC, the temperatures of the first and second stages of hydrogen evolution are 371 and 452 K for KNH_2BH_3 [7]; for $Ca(NH_2BH_3)_2$, they are 373 and 413 K [8], 393 and 443 K [9]; and for $Sr(NH_2BH_3)_2$, they are 331 and 366 K [10].

Note that the data on the thermal decomposition of alkali and alkaline-earth metal amidoboranes obtained by different groups differ greatly because of the dependence of thermal decomposition on both the rate of sample heating and the way of synthesizing the compound (traces of the solvent, the heterogeneity of samples obtained mechanochemically) [1, 5].

In this work, the thermal effects of the decomposition of amidoboranes were determined via drop calorimetry [11, 12]. Unlike DSC, this technique allows us to measure thermal effects at a constant temperature.

EXPERIMENTAL

All operations were conducted in an atmosphere of dry argon in an InertLab 2GB box or using the Schlenk line. Commercial ammonia borane (Sigma Aldrich, 90%) was preliminarily purified by recrystal-lization from dry Et_2O [13]. The purity of the preparation was monitored via XRD and IR spectroscopy. THF was dried over metallic sodium, aged over pre-calcined zeolites, and distilled immediately prior to use. LiH hydrides (Sigma Aldrich, 95%), KH (Sigma Aldrich, 95%), CaH_2 (Sigma Aldrich, 99.99%), SrH_2 (Sigma Aldrich, 95%) were used without further purification. FTIR spectra (KBr pellets) were performed on a IR Prestige-21 Fourier IR spectrophotometer (Shimadzu). Solid-state NMR spectra on ^{11}B nuclei were taken at room temperature on a Bruker AVANCE III 400 MHz instrument at a frequency of 128.41 MHz (^{11}B). Solid samples were centrifuged at 12 kHz with a 4-mm rotor. A 1M aqueous solution of H_3BO_3 was used as a standard. The synchronous thermal analysis (STA) of calcium amidoborane was performed in an argon atmosphere using a Netzsch STA 449 F1 Jupiter unit equipped with a Netzsch QMS 403C Aëolos Quadrosphere mass spectrometer.

Amidoboranes

Amidoboranes were synthesized by reaction of ammonia borane with an appropriate alkali or alkaline earth metal hydride in dried tetrahydrofuran [1, 7, 14]:

$$BH_3NH_3 + MH_n = M(NH_2BH_3)_n + nH_2 \ (M = K, Ca, Sr).$$
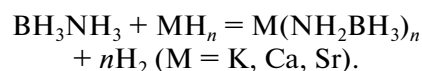
Samples of ammonia borane were dissolved in THF, followed by continuous stirring. A suspension of metal hydride in THF was then added. The reaction mixture was kept at 293 K until the evolution of hydrogen was complete (the amount of evolved hydrogen

was determined volumetrically). The potassium and strontium amidoboranes in THF were insoluble, so the resulting precipitate was washed several times with THF, after which the sample was dried under vacuum for a day at 293 K.

KNH_2BH_3

We used 497 mg (16.1 mmol) of ammonia borane, dissolved in 30 mL of THF, and potassium hydride (633 mg, 15.8 mmol) were suspended in 20 mL of THF. The contents of ^{11}B NMR in d^8-THF were −20.19 and −38.18 ppm (less than 1% impurity KBH_4).

$Ca(NH_2BH_3)_2$

In a flask with hermetic removal, 25 mL of solvent (THF) was added to portions of ammonia borane BH_3NH_3 (501.08 mg, 16.23 mmol) and calcium hydride (370.87 mg, 8.81 mmol). The flask was then placed in an ice bath (273 K), and the reaction proceeded with continuous stirring. Noticeable gas evolution in the system stopped after 11 days. The resulting solution was filtered from the unreacted calcium hydride. The solvent was distilled off in vacuum at 273 K over 7 days. The completeness of THF removal was monitored via mass spectrometry, and no traces of THF in the mass spectrum were observed. The content of solid phase ^{11}B NMR was −17.88 ppm. The sample was stored in a closed flask under argon at 268 K.

$Sr(NH_2BH_3)_2$

We used 500.5 mg (16.2 mmol) of ammonia borane dissolved in 30 mL of THF and strontium hydride with a weight of 721 mg (8.0 mmol) as a suspension in 20 mL of THF. The content of solid phase ^{11}B NMR was −18.23 and −34.09 ppm (less than 1% $Sr(BH_4)_2$ impurity). The solvent was distilled off in vacuum at 293 K.

Calorimetry

In this work, the thermal effects of the decomposition of amidoboranes were determined via drop calorimetry on a DAK1-1a calorimeter with a modified substance input system [11, 12]. Our experiments were performed in an argon atmosphere. Sealed glass ampoules 2−3 cm tall and 1 cm in diameter with wall thickness on the order of 1 mm were used as cuvettes. The heat capacity of each ampoule was measured in blank experiments.

Due to the compounds' sensitivity to atmospheric moisture and oxygen, samples weighing 0.01 mg (Sartogosm MB 210-A) were taken in an InertLab 2GB box under argon atmosphere (water and oxygen content, less than 1 ppm). The samples were placed in glass ampoules that were later evacuated and sealed. The ampoules, which were at room temperature T_0, were successively dropped into a calorimetric cell preheated to temperature T (measurements were made at temperatures of 354, 421, and 483 K). Thermal effect Q of the process was calculated as the difference between measured gross effect Q_0 and heats Q_a and Q_c spent on heating from T_0 to the temperature of the ampoule and substance of the experiment, respectively. The sum of $Q_a + Q_c$ was determined by repeatedly dropping the ampoules filled with material into a calorimetric cell at the same temperature. Since it was shown in [15] that the evolution of hydrogen from $Ca(NH_2BH_3)_2$ at 354 K continues at an appreciable rate after 15 h, each calorimetric experiment was performed immediately at 421 K. Since, according to the tensimetry data in [15], hydrogen evolution continues even after 16 h at 421 K, and 4 mol of hydrogen were released only above 483 K, the heat capacity of the ampule and substance could not be calculated via repeated discharging of the ampoule with the substance. In experiments with $Ca(NH_2BH_3)_2$ at 421 K, the heat capacity of ampoules was determined in blank experiments with the dropping of empty ampoules, and the heat capacity of amidoborane calcium was assumed to be equal to the doubled heat capacity of ammonia borane (75.37 J/(mol K) [16]). The error in this estimate of the heat capacity was assumed to be 30%.

RESULTS AND DISCUSSION

Our results from calorimetric measurements are shown in Tables 1−3. Since the rate of hydrogen evolution from $Ca(NH_2BH_3)_3$ is low at 354 K [15], calorimetric measurements for $Ca(NH_2BH_3)_3$ were made immediately at 421 K. The measured gross heat effects of the decomposition of all the investigated amidoboranes were slightly exothermic (Table 4), which agrees with the data of [7, 10, 17]. According to the data of [9], however, the first stage of the thermal decomposition of $Ca(NH_2BH_3)_2$ is weakly endothermic. Note that the calcium amidoborane used in [9] contained traces of solvent (THF). The authors of [9] noted that THF cannot be completely removed from $Ca(NH_2BH_3)_2$. After evacuation at room temperature for 12 h, approximately 0.1 mol of THF per mole of amidoborane calcium remains. For a sample containing THF, the authors of [9] estimated the thermal effect of decomposition of amidoborane calcium at 363 K as +3.5 kJ/mol; under these conditions, less than 0.3 mol of hydrogen per 1 mol of amidoborane calcium are released.

In contrast to [9], we found that prolonged evacuation (over 7 days) of the sample under vacuum results in the complete removal of THF, as was proved by mass spectrometry. The gross thermal effects of the

Table 1. Results from our drop calorimetry study of KNH_2BH_3

n, mmol	m_a, g	t, h	Q_0, J	T_0, K	$Q_a + Q_c$, J	$-Q$, J	$-\Delta H_T$, kJ/mol
				$T = 354$ K			
0.138	1.0788	4.8	57.0	294.5	57.3	0.3	2.0 ± 2.5
0.267	1.3016	1.4	69.4	293.5	69.9	0.5	1.7 ± 1.6
0.219	1.1547	5.7	60.2	293.5	60.6	0.4	1.9 ± 1.8
						Average	1.9 ± 1.2
				$T = 421$ K			
0.138	1.0788	3.1	95.3	298.0	95.8	0.5	3.7 ± 2.1
0.267	1.3016	3.2	116.2	298.0	116.9	0.7	2.7 ± 1.3
0.219	1.1547	2.6	103.0	297.0	104.7	1.7	7.8 ± 1.4
0.210	1.1600	2.8	103.5	297.0	104.5	1.0	4.8 ± 1.4
						Average	4.8 ± 2.0
				$T = 483$ K			
0.138	1.0788	3.6	125.0	301.0	125.4	0.5	3.4 ± 1.8
0.267	1.3016	3.2	152.2	301.0	153.4	1.2	4.3 ± 1.2
0.219	1.1547	4.1	133.7	302.0	134.5	0.8	3.6 ± 1.2
0.210	1.1600	3.3	134.5	302.0	134.8	0.3	1.5 ± 1.3
0.088	1.0818	4	122.5	303.3	123.0	0.6	6.4 ± 2.9
						Average	3.8 ± 1.8

T is calorimeter temperature; n is the amount of amidoborane in an ampoule; m_a is the ampoule's mass; t is the length of the experiment; and ΔH_T is the change in enthalpy.

Table 2. Results from our drop calorimetry study of $Ca(NH_2BH_3)_2$

n, mmol	m_a, g	t, h	Q_0, J	T_0, K	$Q_a + Q_c$, J	$-Q$, J	$-\Delta H_T$, kJ/mol
				$T = 421$ K			
0.143	0.7368	19.6	65.0	299.4	67.1	2.1	14.3 ± 6.5
0.09	0.8892	18.0	78.8	299.5	79.4	0.6	6.9 ± 8.5
0.106	0.7618	15.0	66.8	300.2	68.1	1.3	12.3 ± 7.2
0.094	0.7798	18.1	68.4	300.4	69.4	0.9	10.0 ± 7.7
0.121	0.7662	14.8	68.2	298.8	69.6	1.4	11.4 ± 6.9
0.134	0.8220	14.0	73.0	299.0	74.6	1.6	12.0 ± 6.8
0.105	0.7621	25.5	68.8	297.0	70.0	1.2	11.4 ± 7.4
						Average	11.2 ± 7.3
				$T = 483$ K			
0.141	0.7918	5.5	95.1	897.8	95.7	0.6	4.0 ± 2.0
0.094	0.7798	4.2	89.8	300.1	90.4	0.7	7.3 ± 2.9
0.134	0.8220	4.2	96.9	297.8	98.2	1.3	9.9 ± 2.2
0.105	0.7621	12.2	88.0	298.3	89.3	1.3	12.5 ± 2.6
						Average	8.4 ± 3.6

decomposition of amidoborane calcium free of THF are exothermic (Table 2).

Note that three effects were observed on the thermograms of all our calorimetric experiments with calcium amidoborane at 421 K (Fig. 1). The first endothermic effect corresponds to the heating of the ampoule with the substance; the second, a prolonged (8–9 h) exothermic effect (thermal decomposition) down to the baseline; and a third endothermic effect is observed after ~2 h (Fig. 1). There was no such endothermic effect in experiments with amidoboranes of potassium and strontium, or in experiments with ami-

Table 3. Results from our drop calorimetry study of $Sr(NH_2BH_3)$

n, mmol	m_a, g	t, h	Q_0, J	T_0, K	$Q_a + Q_c$, J	$-Q$, J	$-\Delta H_T$, kJ/mol
				$T = 354$ K			
0.241	1.179	8.4	62.9	295.0	65.1	2.2	9.0 ± 1.7
0.198	1.0477	8.5	56.3	294.0	59.0	2.7	13.6 ± 1.8
0.192	1.1796	8.2	65.7	293.0	65.9	0.2	0.9 ± 2.0
0.170	1.1835	11.2	64.9	293.0	65.5	0.6	3.7 ± 2.3
0.161	1.3314	14.4	72.1	293.0	73.3	1.2	7.4 ± 2.7
0.206	1.1141	13.1	60.6	293.5	61.5	0.9	4.3 ± 1.8
						Average	6.4 ± 4.5
				$T = 421$ K			
0.241	1.179	16.9	106.6	296.0	107.3	0.7	3.1 ± 1.3
0.192	1.1795	11.6	105.5	298.0	106.5	1.0	5.1 ± 1.7
0.206	1.1141	13.1	100.3	297.5	101.0	0.7	3.4 ± 1.5
						Average	3.9 ± 1.1
				$T = 483$ K			
0.241	1.179	14.3	134.8	302.0	139.7	4.9	20.5 ± 1.2
0.192	1.1796	8.2	136.9	296.0	143.0	6.1	31.7 ± 1.5
0.170	1.1835	6.6	137.1	300.0	140.6	3.6	21.1 ± 1.7
0.206	1.1141	15.7	127.4	301.0	132.6	5.2	25.2 ± 1.9
						Average	24.6 ± 5.2

doborane of calcium at 483 K. Individual integration of the regions of the second and third effects produces values of -4.2 ± 2.3 and 1.5 ± 1.1 kJ/mol, respectively. Perhaps the weak endothermic effect is associated with structural rearrangement accompanied by hydrogen evolution (according to tensimetry, hydrogen continues to be released even after 15 h at 421 K [15]). According to [18], the decomposition of $Ca(NH_2BH_3)_2$ proceeds according to an intermolecular mechanism and is accompanied by the formation of $Ca(NHBHNHBH_3)$ containing the doubly charged anion $[NHBHNHBH_3]^{2-}$.

We also performed an STA of calcium amidoborane, which does not contain traces of THF (Fig. 2). During measurements, 3.53 mg of $Ca(NH_2BH_3)_2$ was heated from 313 to 473 K at a rate of 10 K/min. Two exothermic effects were observed: one at 363 K (-1.4 ± 0.1 kJ/mol) and 433 K (-11.6 ± 0.2 kJ/mol),

Table 4. Gross enthalpy ΔH_T° (kJ per 1 mol of amidoborane) of the serial thermal decomposition of amidoboranes, determined via drop calorimetry

T, K	KNH_2BH_3	$Ca(NH_2BH_3)_2$	$Sr(NH_2BH_3)_2$
354	-1.9 ± 1.2	—	-6.4 ± 4.5
421	-4.8 ± 2.0	-11.2 ± 7.3^a	-3.9 ± 1.1
483	-3.8 ± 1.8	-8.4 ± 3.6	-24.6 ± 5.2

[a] No experiment was performed at 354 K.

accompanied by a weight loss of 1.2% (~0.6 mol of hydrogen) and 1.8% (~0.9 mol of hydrogen per 1 mol of amidoborane), respectively. It is worth noting that the process of mass loss does not stop as the temperature rises (Fig. 2). The total weight loss with heating to 493 K is $8.5 \pm 0.3\%$, which corresponds to the release of 4.21 ± 0.14 mol of hydrogen per mole of amidoborane.

After each series of calorimetric experiments, one of the ampoules was opened in a box under argon and the solid products of decomposition were analyzed via FTIR spectroscopy, solid state ^{11}B NMR, and mass spectrometry. In agreement with [8], the samples after decomposition were X-ray amorphous, making XRD uninformative.

According to the data from solid-state ^{11}B NMR (Fig. 3), after the experiments at 354 K, the intensity of the signal attributed to the BH_3 group (-20, -18, and -18 ppm for the initial KNH_2BH_3, $Ca(NH_2BH_3)_2$, and $Sr(NH_2BH_3)_2$, respectively) was 13–20% of the total integrated intensity, indicating the decomposition of more than 80% of the initial amidoborane. Several broad overlapping signals appear in the ^{11}B NMR spectrum in the range of -50 to 35 ppm, indicating the presence of boron atoms in different environments. The weakly expressed maxima correspond to oligomeric boron-containing forms similar to polyborazines (27 ppm) [19], cyclotriborazane (-11 ppm), and B-(cyclodiborazanyl)aminoborohy-
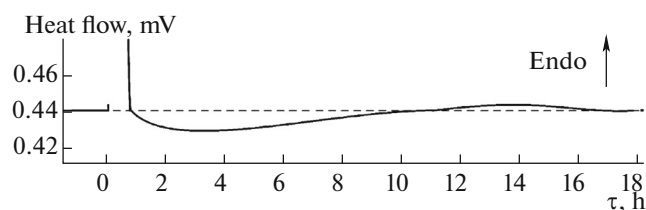
Fig. 1. Thermogram of the experiment with Ca(NH₂BH₃)₂ at 421 K.

dride (−5, −11, and −23 ppm) [20]. In general, our NMR results are inconsistent with earlier observations [7, 21]. However, note that the signal at 24 ppm was observed in ^{11}B NMR KNH₂BH₃ at room temperature [21], indicating that the KNH₂BH₃ used in [21] had already partially decomposed. When heated above 513 K, the signal at 24 ppm predominates [7, 21].

The observed broadening of the bands in the regions of stretching vibrations NH (3100−3450 cm^{-1}) and BH (2190−2480 cm^{-1}) in the FTIR spectra of the samples after calorimetric experiments at 354 and 421 K also indicates the formation of oligomeric or polymer forms, which agrees with the NMR spectroscopy data. An increase in the intensity of signals attributed to the BH group (15−35 ppm) was observed in the ^{11}B NMR spectrum when the temperature of the calorimetric experiment was raised.

According to the mass spectrometry data, solid samples released molecular hydrogen upon heating to 423−503 K after the calorimetric test at 354 K. In contrast, the samples obtained after calorimetric experi-

ments at 421 and 483 K did not produce hydrogen when heated to 623 K.

In the ^{11}B NMR spectrum of Sr(NH₂BH₃)₂, maxima appeared against the background of the wide signal after the experiment at 483 K, indicating local ordering. The much more exothermic (−25 ± 5 kJ/mol) thermal effect at 483 K (Table 4) for Sr(NBH$_x$)₂ could be associated with the ordering of the local environment of boron atoms during the structural rearrangement of the polymer.

CONCLUSIONS

Several products of a polymeric nature are formed in the thermal decomposition of metal amidoboranes, preventing us from attributing the measured gross effect to a specific process. At 354 K, the main contribution (more than 80%) is made by the process

$$M(NH_2BH_3)_x(\text{solid}) = M(NHBH_2)_x(\text{solid}) + xH_2(\text{gas}).$$
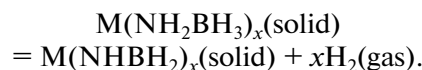
Hydrogen evolution is complete at 421 K with the forming of polymeric, predominantly amorphous M(NBH)$_x$(solid) materials that contain N−H bonds (analogs of polyborazines). The structural rearrangement of polymers occurs at 483 K. Note that the thermal effects of the decomposition of potassium, calcium, and strontium amidoboranes are much less exothermic than the decomposition of the initial ammonia borane (in the first stage, BH₃NH₃ = $1/n$(BH₂NH₂)$_n$ + H₂; ΔH°_{357} = −24.8 ± 2.3 kJ/mol [22]).

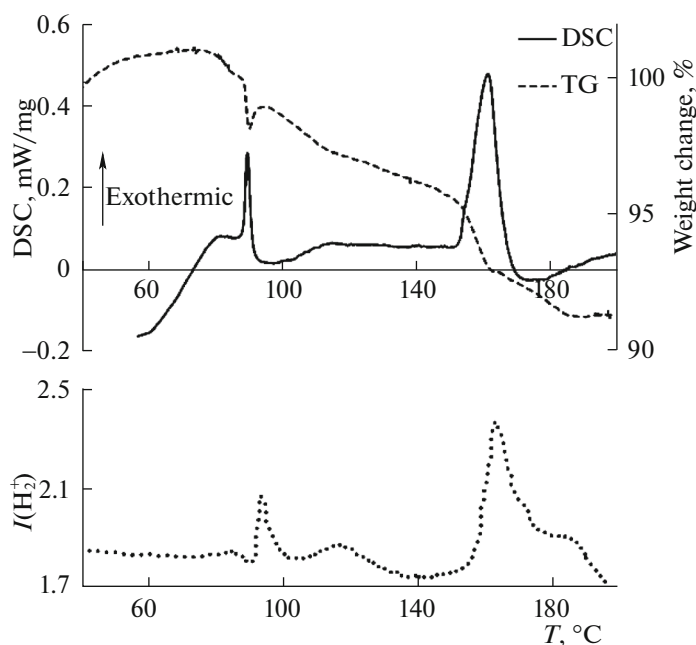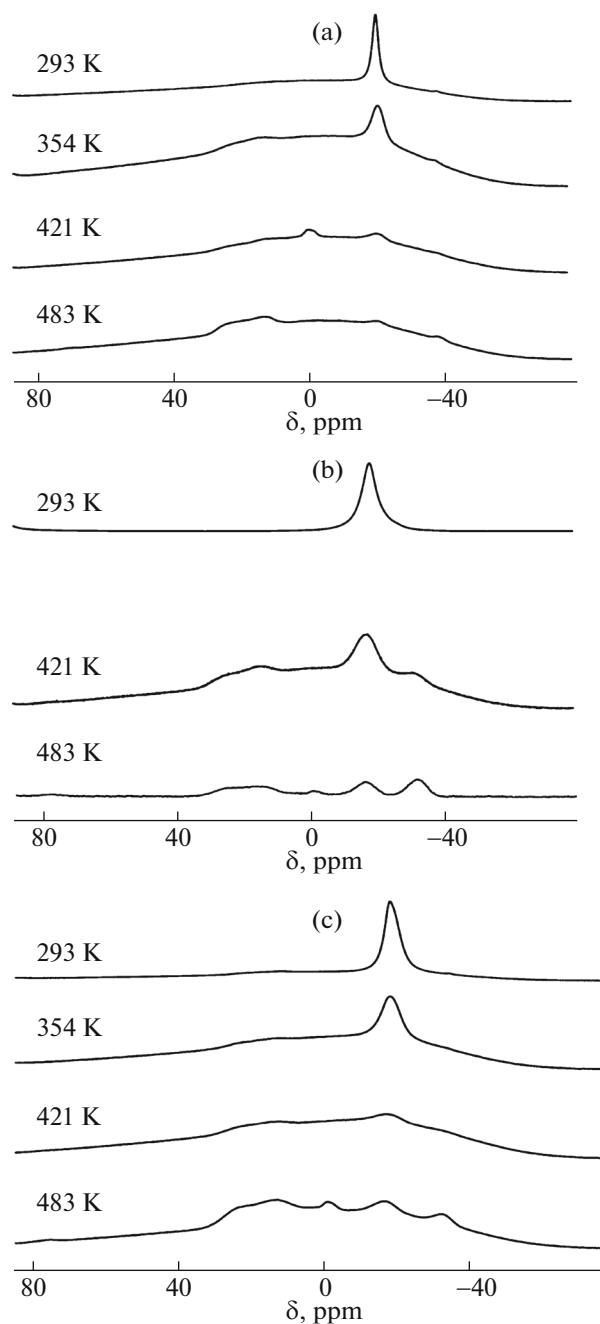**Fig. 2.** Simultaneous thermal analysis of Ca(NH₂BH₃)₂. Heating rate was 10 K/min.

Fig. 3. ^{11}B NMR spectra of the samples after calorimetry experiments at different temperatures: (a) KNH_2BH_3, (b) $Ca(NH_2BH_3)_2$, (c) $Sr(NH_2BH_3)_2$.

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