Sublimation and thermal decomposition of ammonia borane: Competitive processes controlled by pressure

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ABSTRACT

Thermal behavior of ammonia borane BH_3NH_3 (AB) has been studied by calorimetry, tensimetry and mass spectrometry methods. It is shown, that depending on vapor pressure in the system two competitive processes are taking place at 357 K. At atmospheric pressure thermal decomposition with hydrogen evolution is the dominant process: $BH_3NH_{3(s)} = 1/n\,(BH_2NH_2)_{n(s)} + H_{2(g)}$ (1). At low pressures (circa 4 mTorr) the major process is endothermic sublimation of AB: $BH_3NH_{3(s)} = BH_3NH_{3(g)}$ (2). At intermediate pressures both processes occur simultaneously. Enthalpies for the processes (1) and (2) have been determined by drop-calorimetry method: $\Delta_{(1)}H_{357}° = -24.8 \pm 2.3\,kJ\,mol^{-1}$ and $\Delta_{sub}H_{357}°(BH_3NH_3) = 76.3 \pm 3.0\,kJ\,mol^{-1}$. Solid products after sublimation and decomposition have been characterized by IR and NMR spectroscopy; gaseous forms were studied by mass spectrometry. Activation energy of $94 \pm 11\,kJ\,mol^{-1}$ for the process (1) in range 327–351 K was determined by static tensimetry method. Based on the analysis of available thermodynamic characteristics, new values for the standard formation enthalpy of solid AB $-133.4 \pm 5.2\,kJ\,mol^{-1}$ and polyamidoborane $-156.7 \pm 5.8\,kJ\,mol^{-1}$ are recommended.

1. Introduction

Ammonia borane BH_3NH_3 (AB) is prospective hydrogen storage material [1–5]. It has high hydrogen content (19.6% by weight) and undergoes thermally or catalytically induced decomposition with hydrogen evolution [2,4,6–8]. Thermal decomposition of AB has been extensively studied both experimentally [4–6,9–11] and theoretically [9,12]. As revealed by differential scanning calorimetry (DSC) and termogravimetry (TG) methods, AB releases hydrogen in three steps (Scheme 1). The first exothermic step starts at 340 K with formation of polymeric amidoborane $(BH_2NH_2)_n$. The second step starts at circa 380 K with formation of $(HBNH)_n$ [6]. The third step requires much higher temperatures (above 1440 K) and results in hexagonal boron nitride [13].

It was observed that at 363 K the heat effect of AB thermal decomposition depends on the pressure in the system [14]. Decrease of pressure lowers the exothermicity of the first decomposition step, and at pressures lower than 52 mbar endothermic effect was observed [14], presumably due to sublimation of AB. Volatility of AB was noted in 1969, the upper limit of the vapor pressure of AB, determined by effusion method, equals 1 micron at 298 K [15]. Mass spectrometry study by Kuznesof et al. [16] revealed that ion BNH_5^+

has high intensity below 470 K, which indicates presence of gaseous BH_3NH_3 molecules above solid AB. In contrast, in case of introduction of AB to the mass spectrometer via the chromatographic column, BNH_5^+ ions were absent [17].

Using gas phase IR spectroscopy with optical path length of 68 or 92 m, Sams et al. estimated the saturated vapor pressure of AB at 295 K as 10^{-4} Torr [18]. This vapor pressure is enough for the measuring rotation spectra of gaseous AB at room temperature [19] and to purify AB by sublimation [14].

Despite large number of experimental works and reviews devoted to AB [1,2,20], no consistent set of thermodynamic properties for this compound was reported.

Reported standard formation enthalpies of solid AB are $-178.0 \pm 5.9\,kJ\,mol^{-1}$ [21]; -151.9 ± 10.9 [22, as cited in 20]; -153.1 ± 10 [22, as cited in 23]. In ref. [20] value of $\Delta_f H_{298}°$ is erroneously given with the opposite sign. Unfortunately, original reference [22] is no longer available on the internet.

Experimental standard formation enthalpy of gaseous AB is not known. Computed by high level ab initio methods $\Delta_f H_{298}°(AB_{gas})$ equals to $-61.1\,kJ\,mol^{-1}$ at CCSD(T)/CBS level of theory [24,25] and $-49.0\,kJ\,mol^{-1}$ at G3(MP2) level of theory [26]. Recommended value from work [24] is $-56.2 \pm 4.2\,kJ\,mol^{-1}$.

Quantum chemical computations of solid and gaseous AB at DFT level of theory resulted in sublimation enthalpy of AB $76.0\,kJ\,mol^{-1}$ [27] and $90.6\,kJ\,mol^{-1}$ [28]. These values do not include ZPE correction [27]. Since computed in [28] hydrogen elimination enthalpy

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$$BH_3NH_3 \xrightarrow[-H_2]{340\ K} (BH_2NH_2)_n \xrightarrow[-H_2]{380\ K} (BHNH)_n \xrightarrow[-H_2]{1440\ K} BN$$
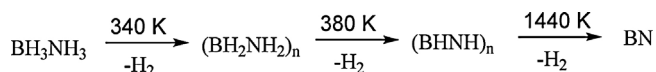
Scheme 1. Thermal decomposition of ammonia borane in the condensed phase.

($+3\ kJ\ mol^{-1}$) is by about $25\ kJ\ mol^{-1}$ more endothermic than the experimental value of $-21.7 \pm 1.2\ kJ\ mol^{-1}$ [43], sublimation enthalpy $90.6\ kJ\ mol^{-1}$ reported in [28] may also be overestimated.

Derived by thermochemical cycle standard sublimation enthalpy $\Delta_{sub}H_{298}^{\circ}$ of AB equals $90.8 \pm 15\ kJ\ mol^{-1}$ [20], $96.7 \pm 10.9\ kJ\ mol^{-1}$ [23], and $121.8 \pm 7\ kJ\ mol^{-1}$ (taking $\Delta_f H_{298}^{\circ}$ values from refs. 21 and 24). Thus, values of sublimation enthalpy of AB, available in the literature, range from 76.0 to $121.8\ kJ\ mol^{-1}$.

Experimental standard entropy S_{298}° of solid AB equals $96.34\ J\ mol^{-1}\ K^{-1}$ [29]. Computed standard entropy of gaseous AB equals $238.9\ J\ mol^{-1}\ K^{-1}$ [24]. Thus, standard sublimation entropy of AB $\Delta_{sub}S_{298}^{\circ}(AB) = 142.56\ J\ mol^{-1}\ K^{-1}$. Based on standard enthalpy and entropy of AB sublimation, vapor pressure of AB computed according to the equation

$$P_{AB} = \exp\left(\frac{-\Delta_{sub}H_{298}^{\circ}}{RT} + \frac{\Delta_{sub}S_{298}^{\circ}}{R}\right)$$

equals 10^{-3}, $3 \cdot 10^{-6}$, and 10^{-11} Torr at $298.15\ K$ (for sublimation enthalpies 76, 90.8, and $121.8\ kJ\ mol^{-1}$, respectively). With the exception of the first value, these saturated vapor pressures are several orders of magnitude lower than the vapor pressure reported in the experiment (circa 10^{-4} Torr at $295\ K$ [18]). Thus, analysis of the thermochemical data available in the literature, indicates that vapor pressure, derived using the value of sublimation enthalpy $76.0\ kJ\ mol^{-1}$ at $0\ K$ [27] is more consistent with experimental vapor pressures. However, as authors [27] state, "Unfortunately there is no experimental sublimation energy available in the literature for comparison". In order to solve this discrepancy, we undertook direct experimental determination of AB sublimation by calorimetry method. Our short preliminary communication has appeared recently [30]. In the present report we present full account of the performed calorimetry experiments and derive consistent set of thermodynamic characteristics for AB.

Another controversial problem for AB decomposition is the activation energy of the first step of thermal decomposition of AB. Kinetic studies of the first step of thermal decomposition of AB revealed S-shaped reaction extent, indicating an autocatalytic mechanism of the hydrogen release [31]. The time of the induction period decreases with the increase of the decomposition temperature, as revealed by volumetric method [32]. Activation energy for the first exothermic step of AB decomposition was estimated using modified Avrami equation as $184 \pm 5\ kJ\ mol^{-1}$ [31]. It should be noted, that decomposition of AB is significantly affected by the environment, as summarized in review [33]. In presence of highly porous silica scaffold SBA-15 activation energy decreases to $67 \pm 5\ kJ\ mol^{-1}$, and exothermicity of the decomposition also decreases from $-21\ kJ\ mol^{-1}$ for pristine AB to $-1\ kJ\ mol^{-1}$ in the scaffold [31]. The decomposition rate of AB and the amount of evolved hydrogen significantly increase in presence of metal organic framework ZIF-8, even at concentration of ZIF-8 as $0.25\ mol\%$ [34]. It was also shown, that AB, infiltrated into the covalent triazine-based framework decomposes at significantly lower temperatures and with much higher reaction rate (1 equivalent of H_2 evolved after $30\ min$ at $85\ °C$) [35].

Measurements of AB decomposition in diglyme [36] yielded activation energy in $65–95\ °C$ range as $113\ kJ\ mol^{-1}$ ($0.25–4\ M$ solutions of AB in diglyme), as monitored by ^{11}B NMR spectroscopy (by disappearance of the signal of AB). However, based on hydrogen evolution rate, activation energy of $154.8\ kJ\ mol^{-1}$ was reported for the same experimental conditions ($4\ M$ solution of

AB in diglyme, $65–95\ °C$). Authors [36] state that "hydrogen generation rate is not directly related to the AB consumption rate", but do not clarify the origin of such a difference. Both activation energies are larger than the donor–acceptor B—N bond dissociation energy of $110.9\ kJ\ mol^{-1}$, computed at CCSD(T)/CBS level of theory [37]. This allowed authors [36] to conclude that B—N bond cleavage plays an important role in determining dehydrogenation pathway.

Recently, Gangal and Sharma [38] performed detailed analysis of the activation energies obtained for the first step of solid AB decomposition. They showed, that activation energy obtained from the DSC measurements using Kissinger equation ($147.5 \pm 23\ kJ\ mol^{-1}$), is significantly overestimated compared to that derived using iso-conversional model ($102 \pm 17\ kJ\ mol^{-1}$). However, a new model, presented by Gangal and Sharma [38], results in even lower value of activation energy: $92 \pm 11\ kJ\ mol^{-1}$.

In order to independently verify activation energy of AB decomposition, we for the first time performed tensimetry study of AB decomposition using static tensimetry method with glass membrane null-manometer [39]. Activation energy of AB decomposition was derived from vapor–pressure – time dependences measured at different temperatures. Solid products were characterized by IR and NMR spectroscopy and gaseous forms were analyzed by mass spectrometry.

2. Experimental details

2.1. Sample preparation

In the preliminary calorimetry experiments, devoted to choosing optimal experimental conditions, commercial BH_3NH_3 (97%, Aldrich) was used as received. However, after the contact with atmospheric air for circa 26 days, powder X-ray study revealed presence of small amounts of $(NH_4)HB_4O_7 \cdot 3H_2O$ as an impurity. Two methods of purification have been used: sublimation and recrystallization from dry Et_2O. Sublimation of AB in vacuum upon heating at $75\ °C$ for two days yielded pure AB as white sublimate in the cold end of the system. However, due to competitive thermal decomposition, the yield of sublimed AB was low (circa 15%). Recrystallization from dry Et_2O after filtration yielded pure AB in circa 70% yield (the Et_2O was removed under vacuum at room temperature). The IR, NMR and X-ray analysis confirmed the purity of AB. Final calorimetry measurements were performed using purified AB, stored at room temperature in sealed under vacuum glass ampoules, which were opened directly prior to use.

2.2. Calorimetry measurements

Drop-calorimetry method, which allows studying thermal effects at constant temperature, was used throughout. Principal scheme of the device is given in Fig. 1. It consists of DAC1-1a differential calorimeter [40] and system for sample dropping. Such a construction allows performing experiments both in vacuum (at circa $4\ mTorr$, controlled by ionization-thermocouple vacuummeter VIT-2) and under atmospheric pressure (circa $760\ Torr$). Calorimetric measurements under inert atmosphere (nitrogen) and under air yielded virtually identical results. Small glass crucible (cylinder with $10\ mm \times 40\ mm$ with walls of $0.5\ mm$ thick) filled with AB was dropped into the calorimetric cell. Heat capacity of each empty crucible C was determined beforehand: $C = Q/(m(c) \cdot \Delta T)$, where $m(c)$ – mass of the crucible (g), Q – measured heat effect (J), and ΔT – difference between calorimeter temperature (K) and temperature of the crucible before dropping.