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Thermochemical investigations on borazane (BH_3–NH_3) in the temperature range from 10 to 289 K

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Abstract

The molar heat capacity of borazane BH_3–NH_3 was determined in the 10–289 K range. Two different adiabatic calorimeter systems, each using the classical heat-step method, were applied for the measurements. The molar standard entropy of borazane at T=298.15 K was determined to be S^0=96.34 J K^{-1} mol^{-1}. For the phase transition at T=224 K, a transition entropy of ΔS=6.87 J K^{-1} mol^{-1} was calculated from the heat capacity data. The results of X-ray powder diffraction confirm an order–disorder transition with a change of the lattice structure from orthorhombic to tetragonal. From low-temperature differential scanning calorimetry, a transition enthalpy of ΔH=1.34 kJ mol^{-1} was found, the transition enthalpy derived from the heat capacity is ΔH=1.48 kJ mol^{-1} © 1998 Elsevier Science B.V.

Keywords: Borazane; Heat capacity; Phase transition; Standard entropy; Transition enthalpy

1. Introduction

The thermochemical properties of the compounds in the boron–nitrogen–hydrogen system are of great interest for various reasons. Numerous theoretical publications are concerned with comparisons of various boron–nitrogen–hydrogen compounds with their isosteric organic analogues. From a more practical point of view, some of these compounds are interesting reducing agents in organic chemistry and potentially useful for applications in the field of energy- and hydrogen-storage systems because of the large amount of hydrogen involved in the synthesis and decomposition of the compounds in this system. Especially for this purpose, the knowledge of thermochemical data is crucial for further investigations.

For one of the basic compounds in this system, borazane or amin-borane, BH_3–NH_3, the molar heat capacity C_p at low temperatures and, thus, the molar standard entropy S^0 is not yet known. A phase transition at approximately T=225 K was first reported by Lippert and Lipscomp [1] in 1956 and more recently confirmed by Hoon and Reynhardt [2] in 1983 and Boese et al. [3] in 1991. Although the nature of the phase transition seems meanwhile well established, no numerical values of the transition enthalpy and entropy are available so far.

In this work, the molar heat capacity of BH_3–NH_3 was determined in the 10–289 K range, and the thermodynamic properties, the molar standard entropy $S^0(T)$ and molar enthalpy difference ΔH^0=$H^0(T)$–

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$H^0(0)$, were derived from these data. The phase transition was additionally investigated by means of X-ray powder diffraction and differential scanning calorimetry.

2. Experimental

The borazane used for the measurements was synthesised from ammonium carbonate and sodium borohydride (chips, Merck) in tetrahydrofurane solution, based on a method described by Hu et al. [4]. The samples used in a respective series were synthesized in different batches. Analysis by X-ray powder diffraction showed no detectable impurities.

The heat capacity measurements were performed in two different adiabatic calorimeter systems. Both work with the classical heat step method and are fully automated. The reliability of the calorimeters was proofed with standard samples and is, in the whole temperature range, better than 1%. One of the applied calorimeters is a simple construction with just one adiabatic shield, based on previously developed low-temperature calorimeters [5]. It is installed in a commercially available refrigerator system and works without the need of liquid helium supply. The calorimeter and the refrigerator system are described in detail in [6]. The sample of 1.26 g borazane was pressed into a pellet before mounting it into the calorimeter. A drawback of the system, which was designed to work with relatively small bulk samples, is the lack of a container for powder substances which could be filled with a heat-exchange gas. Thus, the rapidly increasing thermal resistance in the phase-transition region rendered reliable measurements impossible. The data from this calorimeter, henceforth referred to as Series I, range only from 15 to 185 K.

A low-temperature precision calorimetric system at the Department of Chemistry of the Rijkuniversiteit, Utrecht, [7] was used to perform a second measurement (Series II) over the temperature range from 10 to 289 K. In this calorimeter, a gold-plated copper container was used, which was filled with 2.3099 g of the sample, evacuated and consecutively closed with a helium pressure of ca. 1000 Pa for the heat exchange. In Fig. 1, both series are plotted in the form $C_p=C_p(T)$. The distance of the measured heat capacity points is in both series smaller than 1 K. The coincidence between the two series is very good over the whole range covered by Series I.

Temperature-dependent X-ray powder diffraction studies were carried out in steps of 10 K starting from

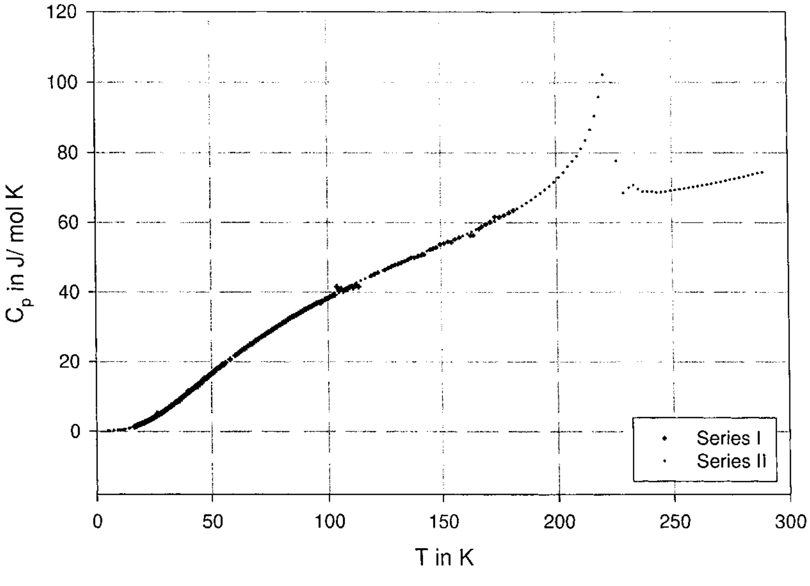

Fig. 1. Molar heat capacity of borazane; experimental data points (C_p-axis clipped).

T=160 K using a Siemens D 5000 diffractometer, supplemented by a Cryojet LT 708 by Oxford Instruments for low-temperature measurements. The DSC curves of the phase transition were obtained by means of a SETARAM DSC 141 in a nitrogen atmosphere.

3. Results and discussion

The thermodynamic properties for borazane were determined by integration of the heat capacity data from Series II only, because of their higher precision. For temperatures <10 K and >289 K, which were not covered by our measurements, an extrapolation is required. Although the low-temperature data above T=10 K cannot be fitted to a function of the form

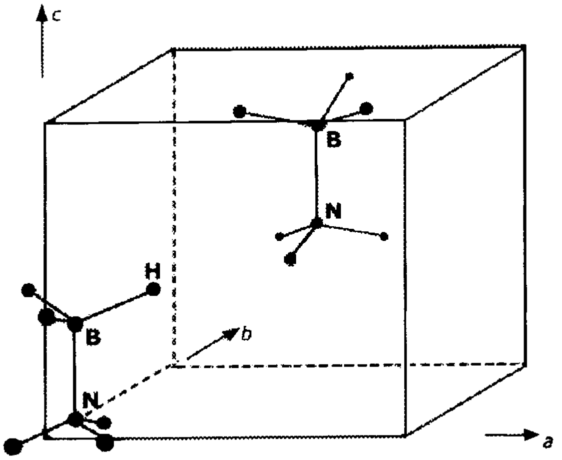

Fig. 2. Unit cell of borazane, after Hoon and Reynhardt [2].

Table 1
Thermodynamical properties for borazane at selected temperatures

T/K	C_p/(J mol^{-1}K^{-1})	C_p/(J mol^{-1}K^{-1})	ΔS^0/(J mol^{-1}K^{-1})	ΔH^0/(kJ^{-1} mol^{-1})
	Series II	Series I		
10	0.448	0.401 [a]	0.113	0.0085
20	2.304	2.348	0.8401	0.0124
30	6.183	6.142	2.457	0.0536
40	11.17	11.17	4.893	0.139
50	16.54	16.58	7.962	0.278
60	21.83	21.72	11.45	0.470
70	26.73	26.46	15.18	0.713
80	31.10	30.87	19.04	1.002
90	35.03	34.83	22.93	1.333
100	38.61	38.30	26.82	1.702
110	41.83	41.46	30.65	2.104
120	44.85	44.70	34.42	2.538
130	47.75	47.69	38.12	3.001
140	50.57	50.52	41.77	3.493
150	53.42	53.30	45.35	4.013
160	56.25	56.07	48.89	4.562
170	59.27	58.77	52.39	5.139
180	62.66		55.87	5.748
190	66.70		59.37	6.394
200	72.08		62.93	7.087
210	79.90		66.63	7.845
220	99.97		70.71	8.724
230	69.17		77.89	10.33
240	68.87		80.85	11.03
250	69.11		83.66	11.72
260	70.20		86.39	12.41
270	71.43		89.06	13.12
280	72.91		91.68	13.84
298.15 [a]	75.37		96.34	15.19

[a] Extrapolated.

Table 2
Structural data from different authors and from the present study

Temperature/K	Structure	Space group	a/Å	b/Å	c/Å	Reference
298	tetragonal	I4 mm	5.235		5.027	[1]
295	tetragonal	I4 mm	5.240±0.005		5.028±0.008	[2]
110	orthorhombic	Pmn 2_1	5.517±0.001	4.742±0.001	5.020±0.001	[2]
160	orthorhombic	Pmn 2_1	5.485	4.857	5.035	present study
200	orthorhombic	Pmn 2_1	5.421	4.945	5.023	[3]

$C_p=\alpha\times T^3$, T^3-behaviour was assumed below T=10 K in order to extrapolate to 0 K. The extrapolation to T=298.15 K is based on the data at temperatures from 240 to 289 K.

In Table 1 are given at rounded temperatures smoothed values of the molar heat capacity C_p together with the determined thermodynamic quantities ΔS^0 and ΔH^0. Both differences represent the value at the corresponding temperature minus the value at 0 K. With the assumption that S^0(0 K) is equal to zero, the ΔS^0-values in Table 1 represent the temperature dependence of the molar standard entropy S^0.

The observed phase transition extends over a wide temperature range and has its maximum in C_p at T=224 K. The transition is confirmed by X-ray studies in the temperature range from 170 K to room temperature. The low-temperature phase was indexed as

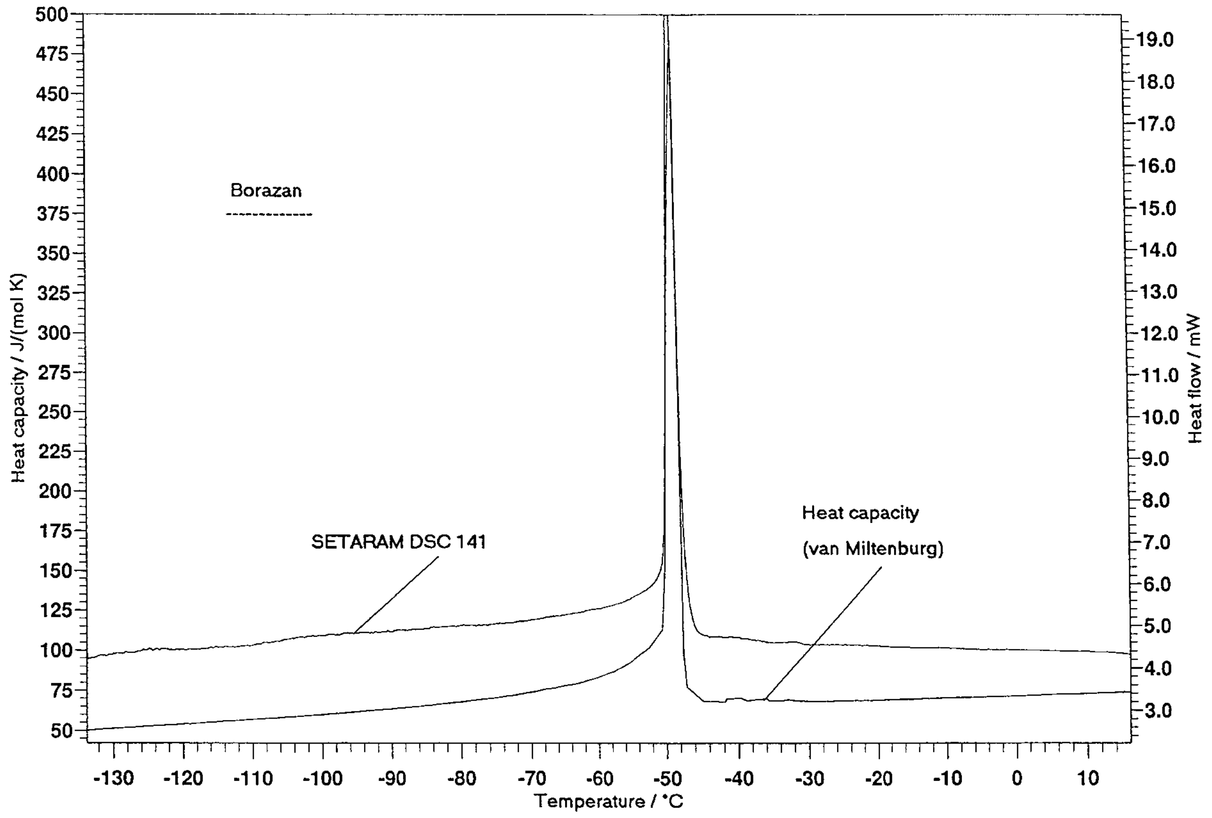

Fig. 3. Phase transition of borazane, comparison between DSC and heat capacity results.

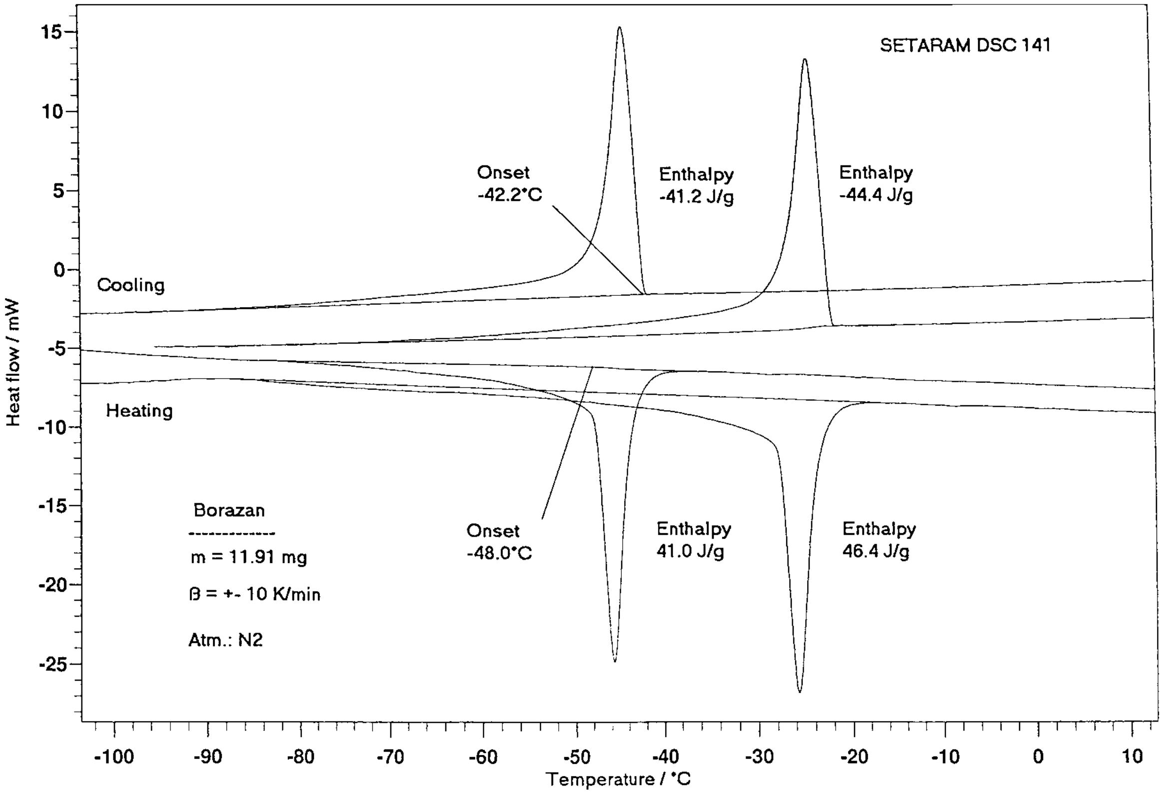

Fig. 4. DSC measurements of the phase transition with the SETARAM DSC 141.

orthorhombic, in agreement with the works of Hoon and Reynhard [3] and Boese et al. [4]. Structural data by the previous workers as well as from the present study are given in Table 2. The *a*-axis of the unit cell shows an anomalous behaviour as it contracts with increasing temperature. This is explained by a model of Hoon and Reynhardt, according to which thermally activated coplanar BH_3- or NH_3 groups execute three-fold reorientations perpendicular to the *c*-axis, or even rotate freely. For illustration, the contents of the unit cell are given in Fig. 2. Geometrical considerations show that this must lead to a reduction in *a*, while *b* increases with increasing reorientation rate. Our observation of a relatively wide range of the phase transition supports this model.

Fig. 3 shows that, in the phase-transition region, the shapes of the heat capacity curve and the heat flow curve obtained in the DSC measurements are very similar. Also, the temperature values of the respective maxima are nearly identical. In both cases, the numerical evaluation of the area under the peak is difficult and depends strongly on the choice of the base lines. In Fig. 4 this problem is illustrated for the DSC curves. For clarity, the peak pair with the higher enthalpy values is shifted arbitrarily on the *x*-axis. This figure also demonstrates that there is virtually no hysteresis between the respective cooling and heating curves.

From the heat-capacity data, the entropy of transition was determined as the difference between the value obtained by direct integration at T=240 K and a hypothetical value without the transition, which was calculated by extrapolation of two functions that were fitted to the experimental heat-capacity data at temperatures <140 K and >240 K, respectively. Assuming the uncertainty of the base line, a value for the molar transition entropy of ΔS=6.87 J mol^{-1}K^{-1} is the result.

Assuming a first-order transition, a direct integration of the heat capacity curve using the low- and high-temperature fits as baseline, leads to a value for the molar transition enthalpy of ΔH=1.48 kJ mol^{-1}. The evaluation of the DSC data delivers, according to the respective position of the baseline, the following values for the molar transition enthalpy:

heating with β=10 K/min: ΔH_1=1.27 kJ mol^{-1} and ΔH_2=1.43 kJ mol^{-1},
cooling with β=10 K/min: ΔH_3=1.27 kJ mol^{-1} and ΔH_4=1.37 kJ mol^{-1},
resulting in a mean value of: ΔH=(1.34$\pm$ 0.02) kJ mol^{-1}.

Considering the diversity of the applied methods and the relatively arbitrary base-line positioning in both cases, the difference of 0.2 kJ mol^{-1} between the two transition enthalpy values seems to be acceptable.

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