

## **THERMODYNAMICS OF PHASE TRANSITIONS AND HEAT CAPACITIES OF MONOSUBSTITUTED *n*-ALKANAMINIUM BROMIDES ABOVE ROOM TEMPERATURE**

*O. Generowicz, L. Lubkowski\* and J. Blazejowski\**

VACUUM ELECTRONICS RESEARCH AND DEVELOPMENT CENTER, 00-241 WARSAW, POLAND; INSTITUTE OF CHEMISTRY, UNIVERSITY OF GDANSK, 80-952 GDANSK, POLAND

Differential scanning calorimetry was applied to examine the thermodynamics of solid-state phase transitions and fusion processes of compounds of the general formula ( $n$ -C<sub>*p*</sub>H<sub>2*p*+1</sub>NH<sub>3</sub>)Br (where  $p = 0-3$ ). The heat capacities of the compounds in the range from ambient temperature to the onset of their volatilization were also studied. All the thermochemical characteristics reveal a dependence on the structure of the alkanaminium cations.

In several earlier papers, we have reported the results of studies on the thermal features of various salts of nitrogen organic bases [1-5]. On the basis of these investigations, we were able to derive basic thermochemical quantities for the pure compounds, i.e. their standard enthalpies of formation and crystal lattice energies, as well as those characterizing their decomposition. Unfortunately, the applied method appeared to be insufficient for quantitative examination of the thermal behaviour of the compounds below the onset of their dissociation and volatilization. This note reports the results of differential scanning calorimetry determinations of heat capacities and enthalpies of solid-state phase transitions and melting for selected *n*-alkanaminium bromides. Despite the investigations undertaken in the past, the knowledge of the latter problems is still incomplete [6-13].

### **Experimental**

All reagents used were of the best available grades. The ammonium bromide was recrystallized from MeOH and finally purified by sublimation [10]. The alkanaminium hydrobromides were synthesized by mixing aqueous

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Akadémiai Kiadó, Budapest*

solutions of amines with an almost stoichiometric amount of hydrobromic acid. The resulting crystals were separated and purified by repeated crystallization from MeOH [7, 14]. Finally, they were separated by filtration and dried in a vacuum desiccator over  $P_2O_5$  in the dark. The identity of the compounds was confirmed by elemental analysis and bromide ion content determination. The enthalpies of transitions were measured on a Du Pont Model 1090 differential scanning calorimeter, in a manner described elsewhere [15], at a scanning rate of  $5 \text{ deg} \cdot \text{min}^{-1}$ . The temperature scale was calibrated by using the melting temperatures of standard compounds. The transitions in several reference materials were used as calibration standards for obtaining enthalpies of transitions [15, 16]. The heat capacity measurements were carried out with standard synthetic sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) as reference material. The temperature step of the measurements was 5 deg. All data reported were obtained from at least three replicate runs.

## Results and discussion

The DSC curve of methanaminium bromide, chosen as an example, is shown in Fig. 1. Table 1 lists information regarding solid-state phase transi-

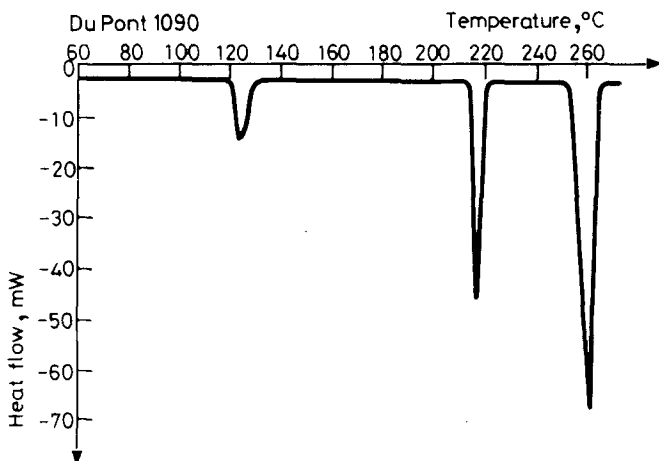


Fig. 1 DSC analysis of methanaminium bromide. Mass of sample = 28.2 mg

Table 1 Phase transition characteristics enthalpies ( $\Delta H$ ) and entropies ( $\Delta S$ ) of transition and heat capacities ( $C_p$ ) of ammonium and alkanaminium bromides

Compound <sup>a</sup>	Character <sup>b</sup>	Phase transitions				Heat capacity <sup>d</sup>	
		Temperature <sup>c</sup> , K	$\Delta H$ , kJ·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta S$ , J·mol <sup>-1</sup> ·K <sup>-1</sup>	$C_p$ , J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta T$ , K	
(NH <sub>4</sub> )Br	$T_r$	$T_0$	$T_P$				
		427.4	430.5	3.01	6.98	a = 64.5	
		412.7 [10]		3.59 [10]	8.71 [10]	b = 0.0814	300-440
						c = -3.71 E-05	
(CH <sub>3</sub> NH <sub>3</sub> )Br	$T_r$		397.7	1.60	4.02	a = 155.1	
				1.28 [7]	3.84 [14]	b = -0.514	300-480
				1.8 [11]		c = 8.70 E-04	
	$T_m$		488.4	3.51	7.18		
			531.9	8.34	15.69		
			537.0 [7]				
(C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> )Br	$T_r$		369.9	12.07	32.63	a = 343.6	
				11.30 [7]		b = -1.69	300-360
				9.6 [11]		c = 3.00 E-03	
	$T_m$		439.5	8.52	19.38		
			434 [7]	8.37 [7]	19.25 [7]		
(n-C <sub>3</sub> H <sub>7</sub> NH <sub>3</sub> )Br	$T_m$		464.6	13.34	28.72	a = 59.4	
			456 [7]	12.51 [7]	27.61 [7]	b = 0.212	300-450
						c = 9.12 E-05	

<sup>a</sup> For names of amines see ref. [1] <sup>b</sup>  $T_r$  = solid-state phase transition;  $T_m$  = melting, <sup>c</sup>  $T_0$  = temperature at onset of DSC peak;  $T_P$  = temperature at maximum of peak, <sup>d</sup> the form of the quadratic equation approximating the experimental  $C_p$  values in the temperature range indicated by  $\Delta T$  is given

tions and fusion processes in the compounds studied, together with heat capacity data.

Solid ammonium and alkanaminium halides undergo a number of phase transitions. The different known phases are usually given Roman numerals (i.e. I, II, III, etc.) or letters of the Greek alphabet (i.e.  $\alpha$ ,  $\beta$ ,  $\gamma$ , etc.), in sequence of decreasing temperature. Ammonium bromide undergoes only one first-order polymorphic transition above room temperature, i.e.  $\text{II} \rightarrow \text{I}$  or  $\beta \rightarrow \alpha$ . The two phases are distinguished by the differences in the interrelation of the orientations of the  $\text{NH}_4^+$  ions and in the relative positions of the ions. The  $\alpha$  phase has the NaCl structure (space group  $\text{O}_h^5$ ), in which the  $\text{NH}_4^+$  ions are orientationally disordered. The  $\beta$  phase has the CsCl-type structure (space group  $\text{O}_h^1$ ), with the  $\text{NH}_4^+$  ions in a state of disorder between two different orientations in the octahedral crystal field [13]. The entropy of the  $\text{II} \rightarrow \text{I}$  phase transition in  $\text{NH}_4\text{Br}$  can be well approximated with the formula:  $\Delta S_{\text{tr}} = R \cdot \ln(\text{number of orientations of the } \text{NH}_4^+ \text{ ion in phase I} / \text{number of orientations of the } \text{NH}_4^+ \text{ ion in phase II})$  [14]. Considering the values of  $\Delta S_{\text{tr}}$  listed in Table 1, it may be suggested that the  $\text{NH}_4^+$  ion in phase I is randomly distributed among 4 to 6 equivalent orientations in the lattice. At room temperature, methanaminium bromide has a tetragonal structure belonging to the space group  $\text{P4/nmm}$  [12]. In this structure, named the  $\alpha'$  phase, the cation is disordered with respect to the orientation of the methyl and also ammonium groups about the C-N bond axis. Just below room temperature, the compound exists in the stable  $\beta$  phase (temperature of  $\beta \rightarrow \alpha'$  transition = ca. 283 K [7, 11, 12]; however, this transition was not recorded in our experiments). Above ca. 390 K, the stable phase is the  $\alpha$  phase [12, 14]. Detailed structural data for other than room temperature are not available. The entropies of phase transitions demonstrate, however, that the polymorphic transformations in  $(\text{CH}_3\text{NH}_3)\text{Br}$  lead to crystal structures of higher symmetries with increasing temperature. Our studies revealed that the DSC peak arising from the  $\alpha' \rightarrow \alpha$  transition exhibits two minima separated by 0.7 deg. Furthermore, we recorded a transition at 485.0 K not previously reported. The entropy of this transition is relatively high, which might suggest that the cation undergoes advanced reorientation in the crystal, as in methanaminium iodide [17]. This high-temperature phase may be considered to be analogous to the plastic phases found in various molecular crystals [17]. Ethanaminium bromide undergoes one phase transition ( $\text{II} \rightarrow \text{I}$ ) above room temperature, at 363 K [11], accompanied by a very high entropy change. One may presume that this

polymorphic transformation brings about a similar reorientation in the crystal to that described above for methanaminium bromide and iodide.

All these alkanaminium bromides melt below the onset of volatilization ( $n = 2$  and  $3$ ) or during the process ( $n = 1$ ). The enthalpies and entropies of fusion show similar features to those of other alkanaminium halides [7, 11]. The experimental molar heat capacity determined for  $(\text{CH}_3\text{NH}_3)\text{Br}$  is shown in Fig. 2.

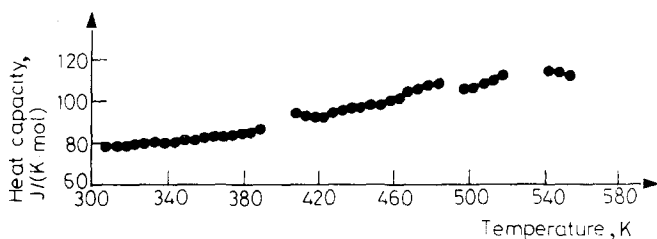


Fig. 2 Temperature dependence of the heat capacity of methanaminium bromide

Similar dependencies were obtained for the other compounds studied. These experimental heat capacities can be fitted well to the polynomial of the second order, namely:

$$C_p(\text{in } \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = a + b \cdot T + c \cdot T^2 \quad (1)$$

Values of constants, together with the temperature ranges over which the experimental data points were approximated, are listed in Table 1. The molar heat capacities increase with both increasing temperature and increasing size of the cation. This latter tendency conforms with the increase in the capacity of the system to store energy. It is also worth mentioning that the heat capacity data, with the exception of those on  $(\text{NH}_4)\text{Br}$  [10], have not previously been reported.

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**Zusammenfassung** — Unter Anwendung von DSC wurde die Thermodynamik von Feststoff-Phasenübergängen und Schmelzvorgängen bei Verbindungen der allgemeinen Formel  $(n-C_pH_{2p+1}NH_3)Br$  (mit  $p=0-3$ ) untersucht. Weiterhin wurde die Wärmekapazität der Verbindungen im Temperaturbereich Raumtemperatur bis Einsatz der Verdampfung untersucht. Alle thermochemischen Eigenschaften lassen eine Abhängigkeit von der Struktur des Alkanaminium-Kations erkennen.