

THERMAL PROPERTIES AND THERMOCHEMISTRY OF ALKANAMINIUM BROMIDES *

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ABSTRACT

The thermal behaviour of unbranched compounds of the general formula $[(C_nH_{2n+1})_pN-H_{4-p}]Br$, with $n = 0$ to 4 and $p = 1$ to 4, was studied by thermoanalytical methods (DTA, TG and DTG). All the compounds examined undergo decomposition upon heating, leading to their total volatilization. In the case of primary, secondary and tertiary amine hydrobromides, the thermal-dissociation process is accompanied by the release of the appropriate amines and HBr to the gaseous phase. Thermogravimetric curves for these derivatives indicate that the process comprises two stages. In both steps thermal dissociation proceeds via the same chemical mechanism; however, each step is determined by different kinetics. Quaternary salts decompose in only one step which is accompanied by the release of the appropriate tertiary amines and bromoalkanes to the gaseous phase. The latter process requires that the remarkable activation barrier be overcome in addition to that resulting from the thermodynamic requirements. On the other hand, the dissociative volatilization of the former derivatives proceeds essentially without any additional barrier over that imposed by the enthalpy change for the reaction. The enthalpies of the thermal dissociation of hydrobromides were evaluated from the non-isothermal thermogravimetric curves, and these values, together with the thermochemical data available in the literature, were used to evaluate the enthalpies of formation and the crystal-lattice energies of the compounds. The crystal-lattice energy was also examined within the Kapustinskii–Yatsimirskii approach, which assumes an additive character of this quantity. The essential thermal and thermochemical characteristics, as well as the influence of the structure of amines on the thermal behaviour of alkanaminium bromides are also reviewed and discussed.

INTRODUCTION

Nitrogen organic bases commonly appear in biological systems either in neat form or as part of a macromolecule. Owing to the presence of a lone electron pair at the nitrogen atom, these compounds can interact, in condensed phases, with Lewis or Brønsted acids forming adducts or salt-type

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derivatives. In biological systems, nitrogen bases often occur in protonated forms that markedly influence their behaviour, e.g. increase their solubility in aquatic media, decrease their volatility. Therefore, the thorough examination of the features of compounds containing protonated forms of nitrogen bases may shed more light on the behaviour of these derivatives in biological systems [1,2]. On the other hand, salts of nitrogen bases are one of the simplest derivatives containing highly unsymmetrical cations. The examination of such derivatives therefore creates an opportunity to reveal the influence of the structure of a cation on the features of the appropriate salts. In the present paper, being a continuation of previous studies [3–6], the thermal properties and thermochemistry of the alkanaminium bromides are reported. Such studies may also be of some practical importance because salts of organic bases are often used in organic synthesis, as catalysts, solvents, etc. [7–12].

EXPERIMENTAL

All reagents used were the best available grades: $[\text{NH}_4]\text{Br}$ (Reachim, U.S.S.R.) and quaternary salts (Fluka AG and Busch SG) of AnalaR grade were used as received. Other alkanaminium bromides were prepared from aqueous solutions of amines by adding a nearly stoichiometric amount of hydrobromic acid or by saturation of solutions of amines in *n*-hexane with gaseous HBr [13–15]. The compounds were purified by recrystallization from absolute ethanol and mixtures of ethanol–ethyl acetate. The identity of the compounds was checked by elementary analysis (performed on a Carlo Erba model 1106 elemental analyser) and by determination of the bromide ion content.

The dynamic thermal analyses were carried out on an OD-103 derivatograph (Monicon) with $\alpha\text{-Al}_2\text{O}_3$ as reference, in a dynamic atmosphere of N_2 . The samples (50 mg) were placed on one platinum plate of the polyplate sample holder [16]. Other operating conditions were as follows: heating rate, ca. 5 K min^{-1} ; sensitivities of DTG, DTA and TG galvanometers, 1/10, 1/1.5 or 1/3 and 50 mg, respectively. The thermogravimetric analyses in quasi-isothermal–isobaric conditions [17], were performed on a Q-1500 derivatograph (Monicon) placing 100 mg samples in a special platinum labyrinth crucible. The samples were heated at a rate of ca. 3 K min^{-1} . The rate of the mass loss was adjusted to 2 mg min^{-1} .

The temperatures T corresponding to the appropriate values of the extent of volatilization α were determined from the TG curves (cf. Fig. 1) in the manner described previously [18]. The range of α over which these data points were taken was chosen by examination of the pattern of all the thermoanalytical curves; it extended over the range where no side reactions

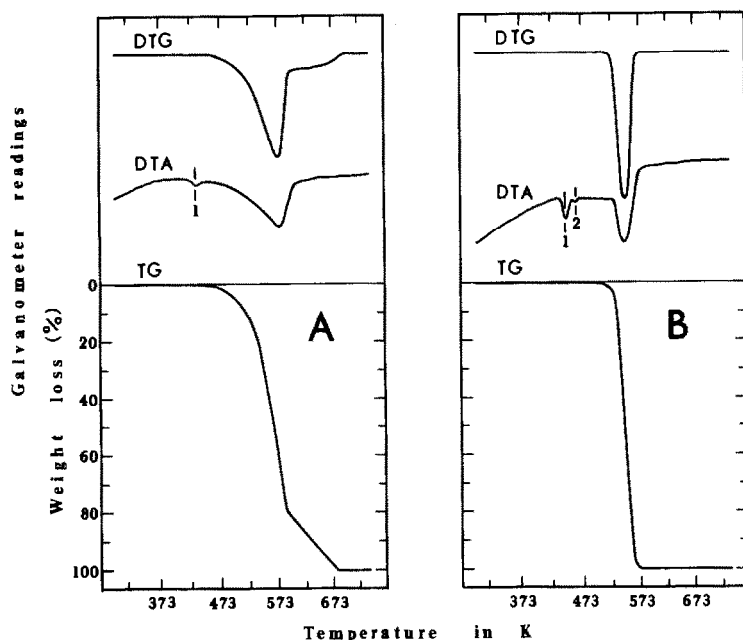


Fig. 1. Dynamic thermal analyses of (A) ammonium and (B) *N,N,N*-triethylethanaminium bromides. (1) Solid-state phase transition; (2) melting.

could be observed. Each α vs. T data point was determined from at least three replicate measurements. An example of a measurement is given in Table 1.

TABLE 1

α vs. T for the volatilization of ammonium bromide (A), *N*-ethylethanaminium bromide (B) and *N,N,N*-triethylethanaminium bromide (C)

α	Temperature (K)		
	A	B	C
0.10	505.4	504.3	531.6
0.18	522.5	515.7	535.1
0.26	533.2	523.8	537.8
0.34	541.5	530.3	540.3
0.42	548.8	535.7	542.5
0.50	554.3	540.3	544.7
0.58	559.1	544.3	546.8
0.66	564.8	551.9	548.9
0.74	570.7		551.4
0.82			553.9
0.90			557.6

RESULTS AND DISCUSSION

General features of the thermal decomposition

The thermoanalytical curves recorded under both dynamic and quasi-isothermal-isobaric conditions for a few chosen compounds are shown in Figs. 1 and 2. To enable further discussion the essential parameters characterizing the thermal behaviour of the compounds studied, derived from the thermal analysis curves, together with the available information from the literature are given in Table 2.

The general feature of the thermal dissociation of all the compounds studied is that they undergo complete volatilization upon heating to 750 K. The dynamic thermogravimetric curves demonstrate, however, that only quaternary salts decompose essentially in one step (see e.g. Fig. 1B). $[\text{NH}_4]\text{Br}$ and all primary, secondary and tertiary alkanaminium salts volatilize in two stages (see e.g. Fig. 1A). The first step, in which up to 80% of the sample volatilizes, is followed by a slow step, seen as a 'tail', in which the remaining fraction of the sample disappears. A similar effect has been observed upon analysis of other alkanaminium salts [3-6] and has been ascribed to certain kinetic phenomena accompanying the volatilization process. We shall discuss this problem later. The interesting point, however, is that the characteristic 'tail' seen in the TG curves of hydrobromides does not occur if analyses are performed in Q-conditions (see e.g. Fig. 2). This additionally confirms that the effect is physical in nature. Complementary studies were also performed in which heating of samples in dynamic conditions was stopped

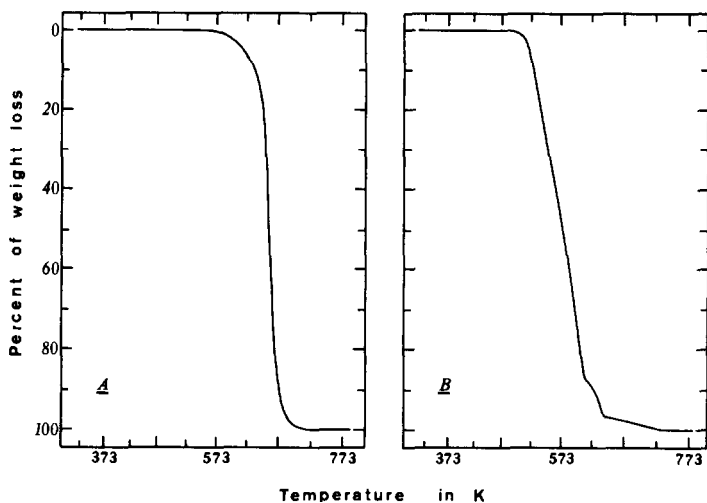


Fig. 2. Quasi-isothermal-isobaric thermogravimetric analyses of (A) ammonium bromide and (B) *N,N*-diethylethanaminium bromide.

just at the beginning of the second stage. The examination of the remaining sample revealed that it had the same composition as the original sample. The dynamic thermoanalytical curves indicate, however, that the volatilization process in the second stage is not simple, particularly in the case of derivatives containing large substituents. For such hydrobromides the shape of the 'tail' is not smooth. Moreover, volatilization of the remainder is accompanied by side processes that are exothermic in nature (see Table 2). These processes have not been studied in detail, although it seems probable that they are of an oxidative origin.

With the exception of $[(\text{CH}_3)_4\text{N}]\text{Br}$, the compounds studied undergo solid-state phase transitions or melting in the range between room temperature and the onset of the volatilization process (Table 2). The literature values of these transition temperatures, if available, compare well with those determined in present study either from the DTA curves or by the standard capillary method. For some compounds, i.e. nos. **11**, **13** and **15**, the effects resulting from fusion were not monitored in the present thermoanalytical experiments. This, presumably, is caused by the fact that these compounds melt when the volatilization process is far advanced.

The temperatures of thermolysis, namely T_p (from DTG and DTA), $T_{0.1}$, $T_{0.74}$ and ΔT , are characteristic features for a given compound; nevertheless, some general trends were revealed. The temperatures characterizing the decomposition of quaternary salts (i.e. T_p , $T_{0.1}$ and $T_{0.74}$) decrease markedly with increasing length of the *n*-alkyl substituent. A similar tendency is rather weak in the case of hydrobromides of primary, secondary and tertiary amines, although a gradual decrease of T_p , $T_{0.1}$ and $T_{0.74}$ values with increasing size of the cation was noted. The ΔT values do not actually show any correlation with the structure of the alkanaminium cation.

The comparison of the characteristic temperatures of the thermolysis of hydrobromides with those of other salts of alkanamines is of interest. In general, bromides volatilize at higher temperatures than do the corresponding chloride salts. On the other hand, the characteristic temperatures of thermolysis of bromides are lower than those of the corresponding hexachlorostannate salts. These trends correlate qualitatively with the stability of alkanaminium salts.

It may, perhaps, be worth mentioning that few works have been devoted to the examination of the thermal properties of alkanaminium bromides [13,21,23,26,34–36,42]. The results of the present study agree well with those of other authors.

Nature of the thermal processes

Owing to the numerous similarities between alkanaminium chlorides and bromides it may be expected that the mechanism of the thermal decomposition of both groups of compounds is the same. This mechanism has been

TABLE 2

The thermal characteristics of the alkanaminium bromides

No.	Formula ^a	Peak temperature ^b (K)			Temperature ^b (K)			Parameters describing the onset of the second stage α	
		DTG	DTA		$T_{0.1}$	$T_{0.74}$	ΔT		
			T_p	T_σ					T_m
1	$[\text{NH}_4]\text{Br}$	565	565	424 °; 411 [20]; 412.7 [21]; 413 [22]; 419 [23]; 427 [24]	505.4	570.7	65.3	0.80	578
2	$[\text{CH}_3\text{NH}_3]\text{Br}$	559	557	395 °; 383 [25]; 385 [26]; 387 [15]; 389 [13]; 394 [24]; 485 °; 485 [24]	517.8	562.1	44.3	0.78	566
3	$[(\text{CH}_3)_2\text{NH}_2]\text{Br}$	553	552	413 °; (406–408) °; 407 [27]	503.8	555.0	51.2	0.81	562
4	$[(\text{CH}_3)_3\text{NH}]\text{Br}$	535	533	446 ° (514–517.5) °; 513 [28]; 516 [27]; 516–518 [29]	494.2	543.3	49.1	0.80	551
5	$[(\text{CH}_3)_4\text{N}]\text{Br}$	650	652		621.8	652.8	31.0		

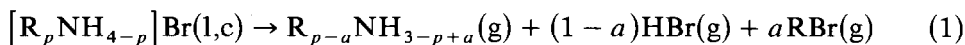
6	$[\text{C}_2\text{H}_5\text{NH}_3]\text{Br}$	542	534 720 (exo)	372 °; 358 [30]; 363 [13,24,25]	438 °; (431–434) °; 419 [30]; 434 [13]; 436 [24]	498.2	0.71	556
7	$[(\text{C}_2\text{H}_5)_2\text{NH}_2]\text{Br}$	541	536 560; 725 (exo)	335 °; 347 °;	492 °; (485–487.5) °; 486 [31]; 486–487 [32]	504.3	0.69	557
8	$[(\text{C}_2\text{H}_5)_3\text{NH}]\text{Br}$	542	541 560; 755 (exo)	448 ° 506 °	519 °; (520–522) °; 520 [31]; 521 [27,33]	500.9	0.71	553
9	$[(\text{C}_2\text{H}_5)_4\text{N}]\text{Br}$	548	547	448 °; 437 [34]; 448 [36] 463 °; 460 [34]; 468 [36]	(558–563) °; 542 [37]	531.6	551.4	19.8
10	$[n\text{-C}_3\text{H}_7\text{NH}_3]\text{Br}$	538	536 560; 660 (exo)		460 °; (451–454.5) °; 455 [38]; 456 [13]; 459 [24]	495.8	0.70	545
11	$[(n\text{-C}_3\text{H}_7)_2\text{NH}_2]\text{Br}$	552	547 575; 725 (exo)		(550–552) °; 544 [39]	506.6	552.5	45.9
12	$[(n\text{-C}_3\text{H}_7)_3\text{NH}]\text{Br}$	509	510 540; 725 (exo)		470 °; (459.5–461.5) °; 453 [39]	476.4	0.74	529
13	$[(n\text{-C}_3\text{H}_7)_4\text{N}]\text{Br}$	515	515	381 °	(555–558) °;	483.6	513.5	29.9

TABLE 2 (continued)

No.	Formula ^a	Peak temperature ^b (K)		Temperature ^b (K)			Parameters describing the onset of the second stage				
		DTG	DTA	T_p	T_o	T_m		$T_{0.1}$	$T_{0.74}$	ΔT	
											α
14	$[(n-C_4H_9NH_2)_3]Br$	551		551 575; 730 (exo)		488 °; (476–478) °; 479 [13]	508.8			0.72	560
15	$[(n-C_4H_9)_2NH_2]Br$	562		559 580; 705 (exo)		(~ 573; D) ° ^c	511.4	565.1	53.7	0.80	570
16	$[(n-C_4H_9)_3NH]Br$	535		550; 735 (exo)		339 °; (334.5–336.5) °; 348 [40]; 348–349 [41]	471.5				
17	$[(n-C_4H_9)_4N]Br$	475	472	365 °; 366–369 [35]; 370 [42] 386 °; 382–383.5 [35]		392.5 [43]; 394.5–395.5 [35]; 395 [42]	450.2	480.1	29.9		

^a For chemical names of amines see ref. 5.^b The symbols were taken from ref. 19: T_p , temperature of the peak; T_o , temperature of the solid-state phase transition; T_m , temperature of melting; T_a , temperature at which the extent of the process is equal to α ; $\Delta T = T_{0.74} - T_{0.1}$.^c From this work. The values in parentheses are the melting points determined by a standard capillary method. D, decomposition.

discussed thoroughly previously with regard to the thermochemistry of alkanaminium chlorides [3,5]. The primary decomposition step is accompanied by a simultaneous release of amine and HBr (RBr in the case of quaternary salts) to the gaseous phase and can be summarized by the equation



where $a = 1$ for quaternary salts and $a = 0$ for the remaining compounds examined.

The interactions between molecules in the condensed phase are fairly well recognized. The interactions are of a similar nature to those that exist in ionic crystals or molten salts. Much less is known about the behaviour of the decomposition fragments in the gaseous phase. Certain experimental facts [44–47], as well as theoretical predictions [47–49] indicate that amine and HBr molecules interact, to some extent, in the gaseous phase forming aggregates. Weak interactions may also occur between gaseous amine molecules [50,51]. All the above-mentioned interactions are rather weak in the temperature range in which the volatilization process was examined. Therefore, it seems justifiable to assume that the dissociation fragments behave, in the gaseous phase, as kinetically free molecules. This forms a useful framework for further thermodynamic and kinetic considerations.

The nature of the processes occurring at higher temperatures has not been studied. Solely on the basis of the thermoanalytical data it may be thought that some processes are of oxidative origin; perhaps, they occur due to the presence of traces of atmospheric oxygen in the reaction zone. However, destruction of the organic fragments of molecules at higher temperatures cannot be excluded.

Thermodynamics of the thermal decomposition

If reaction (1) is realized over a certain temperature range, its enthalpy (ΔH_v) can be evaluated on the basis of the van't Hoff equation assuming that at any stage of the process the system attains thermal equilibrium [3–6]. This implies that the process does not need to overcome any additional energy barrier over that resulting from the thermodynamic requirements. Also other processes, such as the diffusion of gaseous products, side reactions, and so on, cannot influence the volatilization process. The following equation can then be derived

$$\ln \alpha = -(\Delta H_v/2R)(1/T) + (\Delta H_v/2R)(1/T_v) \quad (2)$$

where α is equal to P/P_0 (P is the equilibrium vapour pressure at a given temperature T , and P_0 is the atmospheric pressure), R is the gas constant and T_v represents the volatilization temperature, i.e. the temperature at which P reaches P_0 .

TABLE 3

Thermodynamic and kinetic constants for the volatilization of alkanaminium bromides

No.	Thermodynamic constants ^a		Kinetic constants ^b			
	ΔH_v (kJ mol ⁻¹)	T_v (K)	$g(\alpha - 1) = \alpha$ (R1)		$g(\alpha - 1) = 1 - (1 - \alpha)^{1/2}$ (R2)	
			E (kJ mol ⁻¹)	Z (s ⁻¹)	E (kJ mol ⁻¹)	Z (s ⁻¹)
1	150	580	141	3.2×10^2	159	1.4×10^3
2	223	568	214	1.1×10^6	242	1.3×10^7
3	182	562	173	1.7×10^4	196	1.2×10^5
4	189	549	180	5.6×10^4	203	4.6×10^5
5	(444)	(658)	430	1.8×10^{13}	518	4.0×10^{16}
6	177	557	168	1.2×10^4	188	5.8×10^4
7	188	560	179	3.7×10^4	200	2.1×10^5
8	184	555	175	2.6×10^4	196	1.5×10^5
9	(405)	(555)	396	7.5×10^{14}	471	1.8×10^{18}
10	186	552	177	3.5×10^4	197	1.9×10^5
11	198	563	190	9.5×10^4	213	7.4×10^5
12	186	525	178	1.1×10^5	198	7.3×10^5
13	(277)	(518)	269	5.5×10^9	315	7.6×10^{11}
14	213	559	204	4.8×10^5	227	3.6×10^6
15	180	574	171	9.0×10^3	193	5.7×10^4
16	125	553	117	5.2×10^1	130	1.4×10^2
17	(196)	(487)	189	2.4×10^6	225	1.5×10^8

^a The values of ΔH_v and T_v were evaluated using eqn. (2) and a standard least-squares procedure. In parentheses values for quaternary salts are indicated.

^b The kinetic constants were determined from the equation: $g(1 - \alpha) = (ZT/\Phi)\{\exp[-E_a/(2RT)]\}$. This equation was rearranged to the form $\ln[g(1 - \alpha)/T]$ vs. $1/T$ and values of E_a and Z were derived by using a standard least-squares procedure.

Using experimental α vs. T dependencies the enthalpies of volatilization and T_v values were derived and these are listed in Table 3. Further discussion regarding this matter will be presented in a subsequent paper.

Kinetics of the thermal dissociation

The kinetics of the dissociative volatilization of alkanaminium bromides can be described in the framework of the classical Arrhenius model. This approach requires that only one step in the overall process is a slow one (a bottleneck in the process) and, therefore, that this rate-determining step governs the kinetics of the whole reaction. If a reaction meets the above requirement, the integral kinetic equation takes the form

$$g(1 - \alpha) = (ZT/\Phi) \exp[-E_a/(RT)] \quad (3)$$

which is adequate for the linear temperature-increase conditions [52]. In eqn. (3), $g(1 - \alpha)$ represents the kinetic model for the process (i.e. from the

physical point of view the reaction pathway), Φ is the heating rate, Z is a constant and E_a represents the activation barrier for the reaction. In our kinetic considerations, we used a somewhat modified form of eqn. (3) holding factor 2 in the exponential term (see Table 3). This modification accounts for the fact that the transition state for the dissociative volatilization of the compounds studied is a loosely bound complex of amine and HBr (or RBr) molecules. In such a case, the Arrhenius equation can be considered against two molecules of gaseous products released from the simplest structural unit of the bromide molecule [53].

Using experimental α vs. T dependencies the kinetic constants were derived from eqn. (3), for two reaction models, namely: zero kinetic order model (R1) and surface contracting area model (R2) [18] and these are presented in Table 3. These two models were chosen because they seemed to correspond best to the nature of the process and conditions of its realization. Moreover, these models have been considered in the past for the description of the kinetics of volatilization of some ammonium salts [54–56].

Examination of kinetic constants listed in Table 3 reveals that the E_a values for the R1 model are always slightly lower than ΔH_v values, whereas the kinetic-energy barriers corresponding to the R2 model always somewhat exceed the corresponding ΔH_v values. If this simple approach would indeed describe the kinetic phenomena it would mean that the dissociative volatilization of hydrobromides of amines would not actually require an additional energy barrier over ΔH_v to be overcome. This does not, however, apply to the quaternary salts studied. The enormously high ΔH_v and E_a values for these derivatives indicate that their decomposition proceeds through a mechanism which differs from that characteristic for hydrobromides. The reaction pathway on which quaternary salts dissociate to tertiary amines and RBr requires a noticeable activation barrier over the ΔH values for the reaction to be overcome. This latter conclusion results from the comparison of energy barriers derived in this work (Table 3) with the ΔH values for the decomposition of quaternary salts determined from the known enthalpies of formation of bromide salts (Table 4), amines and bromoalkanes [57]. It can be noted that, in general, the elimination of either HBr or RBr from alkanaminium bromides characterizes comparable thermodynamical barriers. Similar regularities have been found for alkanaminium chlorides and hexachlorostannates [5,6].

The Arrhenius equation (3) fits fairly well the experimental thermogravimetric data in the first step of volatilization. The question arises of how to explain the existence of the second stage in the process, seen as a tail in the TG curves of some of the compounds studied [see e.g. Fig. 1(A)]. The semiquantitative explanation of this effect provides the Jacobs and Russell–Jones approach to the dissociative volatilization processes [55]. This subject has been discussed in several previous works [3–6,58]. From the present knowledge of the problem, it is concluded that a decrease in the rate

TABLE 4

The thermochemical characteristics (in kJ mol^{-1}) of the alkanaminium bromides at 298 K ^a

Substance	ΔH_v^0		$\Delta H_{f,c}^0$		U^0		
	This work	From the literature ^b	This work	From the literature ^b	This work ^c		From the literature ^b
					A	B	
[NH ₄]Br	164	184 [61] 185 [44] 187.9 [62] 188 [23] 189 [21,63,64] 190 [65]	-245	-270.5 [68] -270.8 [14]	654	670	615 [75] 632 [76] 633 [77] 644 [78] 658, 665 [79] 661 [14] 682 [68]
[MeNH ₃]Br	242		-300 (-249)	-258.9 [14]	684 (635)	616	629 [14]
[Me ₂ NH ₂]Br	195		-247	-257.3 [14]	610	603	605 [14]
[Me ₃ NH]Br	208		-267	-253.7 [14]	609	576	579 [14]
[Me ₄ N]Br	(209)		(-268)	-251.5 [14]	(587)	558	494 [80] 544 [81] 553 [14]
[EtNH ₃]Br	203		-286	-294.8 [70]	633	614	633, 677 [70]
[Et ₂ NH ₂]Br	209		-317	-316.5 [70]	607	591	590, 659 [70]
[Et ₃ NH]Br	206		-334	-350.5 [70]	578	578	582, 633 [70]
[Et ₄ N]Br	(205)		(-360)	-374 [71] -377 [70]	(555)	556	612 [70]
[<i>n</i> -PrNH ₃]Br	201		-306		625	613	
[<i>n</i> -Pr ₂ NH ₂]Br	204		-355		593	584	
[<i>n</i> -Pr ₃ NH]Br	200		-396		562	558	
[<i>n</i> -Pr ₄ N]Br	(196)		(-442)		(532)	530	423 [80] 493 [81]
[<i>n</i> -BuNH ₃]Br	227		-354		649	616	
[<i>n</i> -Bu ₂ NH ₂]Br	186		-378		571	593	
[<i>n</i> -Bu ₃ NH]Br	137		-394		494	520	
[<i>n</i> -Bu ₄ N]Br	(86)		(-415)		(453)	506	

^a Values obtained by extrapolation or estimated are given in parentheses.^b References given in square brackets.^c A, values determined from the thermochemical cycle; B, values evaluated from the Kapustinskii–Yatsimirskii equation (using $r_{\text{Br}^-} = 0.196 \text{ nm}$ [60,74] and modifying values of r_{K} from ref. 66 relative to $r_{\text{Cl}^-} = 0.181 \text{ nm}$ [60,74]).

of the mass loss begins at the end of the process when the dimensions of the drops or crystals become relatively small. The non-continuous change in the rate of volatilization, at the beginning of the second stage, may indicate the occurrence of some physical phenomena such as the cracking of a thin layer of liquid substance covering the bottom of the sample holder and the formation of small drops. The diminution of the rate of the process is a consequence of an increase in the cohesive forces in the volatilized material.

Thermochemical characteristics

As has been demonstrated previously several thermochemical characteristics of alkanaminium salts can be derived on the basis of certain literature information and can be evaluated from the TG curve enthalpies of volatilization of the salts [3–6]. These interesting quantities can be determined on the basis of Hess' law. The various relations between the thermochemical quantities are usually presented in the form of a thermochemical cycle. Such a cycle for alkanaminium chlorides has been presented elsewhere [3]. The relations resulting from this cycle are also adequate for bromide salts and are presented below in eqns. (4) and (5).

$$\Delta H_{f,c}^0[(R_pNH_{4-p})Br] = \Delta H_{f,g}^0[R_pNH_{3-p}] + \Delta H_{f,g}^0[HBr] - \Delta H_v^0 \quad (4)$$

$$U^0[(R_pNH_{4-p})Br] = \Delta H_{f,g}^0[R_pNH_{4-p}^+] + \Delta H_{f,g}^0[Br^-] - \Delta H_{f,c}^0[(R_pNH_{4-p})Br] - 2RT \quad (5)$$

All magnitudes in eqns. (4) and (5) refer to 298 K and 1 atm, ΔH_f^0 denotes the enthalpy of formation of a given species ($p = 1$ to 3) and $U^0 + 2RT$ is the lattice enthalpy (U^0 represents the lattice energy). The meaning of the other symbols has been given earlier.

The enthalpies of volatilization derived from eqn. (2) do not refer to 298 K. Therefore, they were modified by using the following equation

$$\Delta H_v^0 = \Delta H_v + \Delta H_{fm}^0 + \sum \Delta H_{\sigma}^0 - \int_{298}^T \Delta C_p^0 dT \quad (6)$$

where ΔH_{fm}^0 is the enthalpy of fusion, the term $\sum \Delta H_{\sigma}^0$ arises from any polymorphic transitions which these compounds may undergo between 298 K and the onset of fusion or volatilization, while $\int_{298}^T \Delta C_p^0 dT$ accounts for the change in enthalpy resulting from changes in the heat capacities of reactants. The enthalpies of solid-state transitions were either taken directly from the literature [13,21,22,24–26] or were estimated. The estimated values were obtained by comparing the areas of the DTA peaks resulting from different phase transitions or volatilization processes and using literature values of the heats of transitions or volatilization, or the ΔH_v values listed in Table 3. The enthalpies of fusion were also taken from the literature, when available [13,24], or were estimated using an empirical relationship relating

to the entropy of fusion: $\Delta S_{\text{fn}}^0 = \Delta H_{\text{fn}}^0/T_m = \text{constant}$. The value of ΔS_{fn}^0 was assumed to be $18 \text{ J mol}^{-1} \text{ K}^{-1}$ on the basis of the available ΔH_{fn}^0 and T_m values for several hydrobromides of amines [13,24]. For ammonium and methanaminium bromides the magnitude of the heat capacity term was estimated to be ca. -6.0 kJ mol^{-1} . This value was obtained within the temperature range 298–500 K using available heat capacity data for $[\text{NH}_4]\text{Br}$ and $[\text{CH}_3\text{NH}_3]\text{Br}$ [21,24], and appropriate gaseous decomposition fragments [59,60]. For the other compounds studied the value of the heat capacity term was assumed to be the same. The validity of this assumption may be gauged from the fact that the expected increase in the heat capacity caused by an increase in the size of an alkyl group should be similar for both the salts and the corresponding amines. Furthermore, volatilization of all amine hydrobromides begins at roughly the same temperature. The modified values of ΔH_{v}^0 are listed in Table 4.

To evaluate the thermochemical quantities from eqns. (4) and (5) we used values of the enthalpies of formation of the gaseous amines and corresponding alkanaminium cations from ref. 66. Furthermore, values of $\Delta H_{\text{f,g}}^0[\text{HBr}]$ and $\Delta H_{\text{f,g}}^0[\text{Br}^-]$ were assumed to be equal to (in kJ mol^{-1}) -34.6 [60,67] and -219 [60,67–69], respectively. The $\Delta H_{\text{f,c}}^0$ and U^0 values derived for the hydrobromides of ammonia and primary, secondary and tertiary amines studied are shown in Table 4.

The values of the standard enthalpies of formation and the crystal lattice energies derived from the thermochemical cycle demonstrate interesting trends against the number p of alkyl substituents R (Fig. 3). With the exception of the ammonium bromide, values of $\Delta H_{\text{f,c}}^0$ decrease linearly with an increase in the number of R in the amine molecule in the range $p = 1$ to

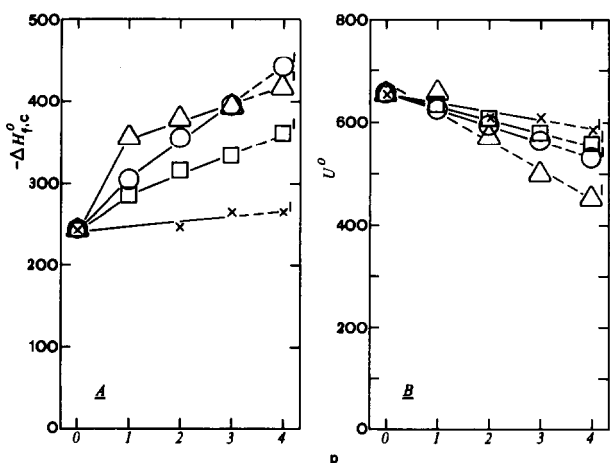


Fig. 3. Enthalpies of formation (A) and crystal-lattice energies (B), both in kJ mol^{-1} , for $[(\text{C}_n\text{H}_{2n+1})_p\text{NH}_{4-p}]\text{Br}$ versus the number of alkyl groups p : \times , $n = 1$; \square , $n = 2$; \circ , $n = 3$; Δ , $n = 4$. The values for the quaternary salts ($p = 4$) were obtained by extrapolation.

3. Similarly, the values of U^0 decrease linearly, although in this case in the range of $p = 0$ to 3. Trends similar to those described above have been observed for other alkanaminium salts [5,6,14,70]. This clearly indicates that both $\Delta H_{f,c}^0$ and U^0 exhibit the features of additive quantities. Therefore, it can be expected that the observed linear dependencies are extended to the quaternary salts. The obtained by extrapolation values of both quantities for the latter compounds are shown in Fig. 3 and in Table 4.

Examining values of $\Delta H_{f,c}^0$ and U^0 , however, it may be noted that the trends observed for the butanaminium salts differ somewhat from those for other compounds. This, presumably, is the characteristic feature of this group of derivatives. In addition, the values of both quantities for methanaminium bromide do not correlate with the rest of the data. This latter discrepancy is brought about by the unexpectedly high ΔH_v value derived for $[\text{CH}_3\text{NH}_3]\text{Br}$ from the dynamic TG curves (Table 3). The possible explanation of this fact might be that the volatilization of the compound requires that a kinetic barrier which is higher than ΔH_v be overcome. For this reason values of both $\Delta H_{f,c}^0$ and U^0 were neglected in the extrapolation procedure. On the other hand, values obtained for methanaminium bromide by extrapolating the curves are indicated (in parentheses) in Table 4. As was mentioned earlier, the remarkable activation barriers for the decomposition of quaternary salts make impossible the direct evaluation of the enthalpies of the reaction. The values of this quantity can be estimated, however, on the basis of known values of the enthalpies of formation of bromoalkanes [57], appropriate tertiary amines [66] and values of $\Delta H_{f,c}^0$ for quaternary salts obtained by extrapolation (Table 4). These estimated values are shown, in parentheses, in Table 4. The comparison of the estimated values of the enthalpies of the thermal dissociation with those derived from the thermogravimetric curves (Table 3) demonstrates that the latter values exceed the expected ΔH_v values by more than 80 kJ mol^{-1} . This fact strongly supports the concept of the existence of the kinetic barrier for the elimination of bromoalkanes from alkanaminium bromides. Similar features are exhibited by other alkanaminium salts [5,6].

Further insight into the crystal-lattice energy problems was possible on the basis of the Kapustinskii–Yatsimirskii approach [72,73]. According to the authors, the lattice energy of ionic crystals can be approximated by using the equation

$$U = 120.2 \left[(\Sigma n) Z_K Z_A / (r_K + r_A) \right] \\ \times \left[1 - 0.0345 / (r_K + r_A) + 0.087 (r_K + r_A) \right] \text{ (kJ mol}^{-1}\text{)} \quad (7)$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule, Z_K and Z_A are the numerical values of the charges of the cation and anion, respectively and r_K and r_A are the ‘thermochemical’ ionic radii (in nm); the evaluated values of U are listed in Table 4.

The values of the crystal-lattice energy determined from the thermochemical cycle compare well with those obtained from the Kapustinskii–Yatsimirskii approach in the case of ethanaminium and propanaminium salts. For ammonium and methanaminium bromides, eqn. (7) predicts somewhat lower values than those derived from the thermochemical cycle, whereas for butanaminium salts the tendency is reversed. Despite these discrepancies, the agreement between the two sets of data is quite good considering that they were obtained in two independent ways. This fact strengthens the reliability of the characteristics derived in this work. The agreement also indicates that the ‘thermochemical’ radii for alkanaminium halogenides exhibit features of additive quantities.

CONCLUDING REMARKS

The enthalpies of formation of crystalline alkanaminium bromides derived in this work correlate quite well with the literature values which were determined from calorimetric measurements (Table 4). Major discrepancies are only seen in the case of first two representatives of the series, namely ammonium and methanaminium bromides. The observed differences may be partially due to the fact that the method applied is actually a non-equilibrium technique. This may cause the experimental ratio of P/P_0 (equal to α) to be somewhat lower than that corresponding to the equilibrium conditions at a given temperature. The form of eqn. (2) indicates, however, that this effect would predominantly influence T_v values. Another source of discrepancy is the imperfect behaviour of the decomposition fragments in the gaseous phase. This issue was discussed earlier in the text. If amine and HBr remain undissociated during the volatilization process and in the gaseous phase, all ΔH_v values would be equal only in half of those listed in Table 3. The comparison of the present data with literature values reveals, therefore, that the assumption of the complete dissociation of $R_pNH_{4-p}^+ \dots Br^-$ upon volatilization was well fulfilled in the present experiments.

The examination of the data in Table 4 demonstrates that the values of the crystal-lattice energy decrease gradually with increasing size of the alkanaminium cation, i.e. with an increase in the both length of the alkyl substituent and the number of substituents at the nitrogen atom. This decreasing tendency is, however, very weak in comparison with that which would be expected from the changes in the actual size of the cations. To explain this phenomenon it should be remembered that the major contribution to the lattice energy of ionic substances is brought about by electrostatic interactions between the charged centres. In alkanaminium bromides the centres of positive and negative charges are located at the nitrogen and bromine atoms, respectively [82]. Therefore, the distance between these

latter centres should affect predominantly the energy of electrostatic interactions and, thus, the crystal-lattice energy. As revealed by the crystallographic data for hydrobromides of nitrogen organic bases, the $-N \geq H \dots Br$ distance is roughly equal to 0.33 nm in various salts and is affected only very insignificantly by the actual size and structure of substituents [83–86]. Therefore, it can be expected that the crystal lattice energy of the bromide salts of nitrogen organic bases is not affected markedly by the size and structure of the alkanaminium cation. This qualitative explanation could be strengthened by calculating the electrostatic part of the crystal-lattice energy from known crystal structures of the compounds. Preliminary studies in this field fully confirm the main points of the above discussion [87].

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