Thermochimica Acta, 165 (1990) 31–48
Elsevier Science Publishers B.V., Amsterdam

THERMAL PROPERTIES, THERMOLYSIS AND THERMOCHEMISTRY OF ALKANAMINIUM IODIDES *

PAWEŁ DOKURNO, JACEK ŁUBKOWSKI and JERZY BŁAŻEJOWSKI

Institute of Chemistry, University of Gdańsk, 80-952 Gdańsk (Poland)

(Received 21 December 1989)

ABSTRACT

The thermal features of unbranched compounds of general formula $[(C_nH_{2n+1})_pNH_{4-p}]I$, with $n = 0$–4 and $p = 1$–4, were studied by thermoanalytical methods (DTA, TG, DTG and Q-TG). All the compounds studied undergo decomposition upon heating, leading to their total volatilisation. In the primary step of the thermal dissociation of these derivatives, HI or RI, in the case of quaternary salts, and the appropriate amines are released in the gaseous phase. This simple thermal decomposition pattern is usually complicated by secondary reactions of an oxidative nature. The latter processes most probably originate from the thermal instability of HI, which can spontaneously decompose to H_2 and I_2 giving iodine molecules of high oxidative potential.

The enthalpies of the thermal dissociation were estimated on the basis of the van't Hoff equation using dynamic thermogravimetric curves. Values derived in this way were used together with available literature data to evaluate the enthalpies of formation and the crystal lattice energies of the hydriodides studied. The crystal lattice energy problems were also examined within the Kapustinskii–Yatsimirskii approach. An attempt was made to describe the kinetics of the thermal decomposition by adopting an Arrhenius model. The influence of the structure of the amines on the thermal behaviour of their iodide salts is reviewed and thoroughly discussed.

INTRODUCTION

Nitrogen organic bases are constituent parts of many biological systems either in neat form or as fragments of macromolecules. The behaviour of these derivatives is predominantly determined by the presence of a lone electron pair at the nitrogen atom. This lone electron pair imparts basic properties to these molecules. Many features of nitrogen organic bases result from the possibility of their interaction with numerous inorganic or organic acids. Such interactions are made possible by the formation of a strong hydrogen bond between nitrogen and proton. Nitrogen atoms of organic

---

* Presented in part at the 5th Polish Seminar of Thermal Analysis to the Memory of St. Bretsznajder, September 1989, Płock, Poland [1].

0040-6031/90/$03.50

bases may also participate in hydrogen-type bonds that are weaker, than those described above. Moreover, molecules of nitrogen organic bases and those that have electron vacancies may take part in electron-donor–acceptor interactions. All the interactions mentioned above are important for understanding the activity and behaviour of these derivatives in biological systems.

In the past, much attention has been devoted to the nature of the hydrogen bonds in which nitrogen bases are involved [2–9]. Several of our previous works have been essentially concerned with this problem [10–12]. Their aim was to reveal the influence of the structure of a nitrogen-base cation on the thermal features and thermochemistry of salts containing simple inorganic anions: Cl^-, Br^- and $SnCl_6^{2-}$. The present paper, which is a continuation of these studies, reports on the thermolysis and thermochemistry of alkanaminium iodides.

The choice of salts containing a large spherical ion, i.e. I^-, for the investigations creates an opportunity for the comparison of the properties of halogenide salts in the chloride–bromide–iodide series. However, hydriodides differ somewhat from chloride and bromide salts because the enthalpy of formation of HI(g), which is expected to be one of the thermal dissociation products, is positive ($\Delta H^{\ominus}_{f,298}[HI] = 26.5$ kJ mol^{-1}), whereas the enthalpies of formation of HCl and HBr are both negative ($\Delta H^{\ominus}_{f,298}[HCl] = -92.3$ kJ mol^{-1} and $\Delta H^{\ominus}_{f,298}[HBr] = -36.4$ kJ mol^{-1}) [13,14]. Therefore HI, unlike HCl and HBr, can decompose spontaneously into its constituent elements. Because iodine has an oxidative potential similar to that of gaseous O_2 ($I_2/I^- = 0.535$ V and $O_2/OH^- = 0.401$ V [15]), it can act as an oxidising agent towards organic fragments of molecules. Thus, iodides should exhibit unique properties among halogenide salts of nitrogen organic bases.

EXPERIMENTAL

All the reagents used were of the best available grades: $[Me_4N]I$, from BDH Chemicals Ltd., $[Et_4N]I$ and $[n\text{-}Pr_4N]I$, both from Fluka AG and Busch SG, and $[n\text{-}Bu_4N]I$, from Merck, were all of AnalaR grade and were used as received. NH_4I, from P.O.Ch., Poland, was recrystallised twice from MeOH. Most of the compounds studied were prepared by mixing an aqueous solution of the appropriate base with an almost stoichiometric amount of hydriodic acid. The resulting crystals were separated and purified by repeated recrystallisations from MeOH [6,8,16,17]. The hydriodides of *N*-propylpropanamine, *N*,*N*-dipropylpropanamine, *N*-butylbutanamine and *N*,*N*-dibutylbutanamine were synthesised by saturating solutions of the amines in *n*-hexane with gaseous HI [18]. All the compounds were dried and kept in a vacuum desiccator over P_2O_5 in the dark. The identity of the compounds was checked by elemental analysis (performed on a Carlo Erba model 1106 elemental analyser) and by determination of the iodide ion content.

The dynamic thermal analyses were carried out on an OD-103 derivatograph (Monikon) with α-Al_2O_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 [19]. Other operating conditions were as follows: heating rate approx. 5 K $\min^{-1}$; sensitivities of DTG, DTA and TG galvanometers, $\frac{1}{10}$ or $\frac{1}{5}$, $\frac{1}{1.5}$ or $\frac{1}{3}$ and 50 mg, respectively. The thermogravimetric analyses in quasi-isothermal-isobaric conditions [20] were performed on a Q-1500 derivatograph (Monikon) with 100 mg samples in a special platinum labyrinth crucible. The samples were heated at a rate of around 3 K $\min^{-1}$. The rate of mass loss was adjusted to 1 mg $\min^{-1}$.

The temperatures corresponding to the appropriate values of the extent of volatilisation, α, were determined from the TG curves (see Fig. 1) in the manner described previously [21]. The range of α over which these data points were taken was chosen by examination of both the TG and DTG curves; it extended over the range in which smooth shapes, indicating simple one-step decomposition, were observed. Each α versus T data point was

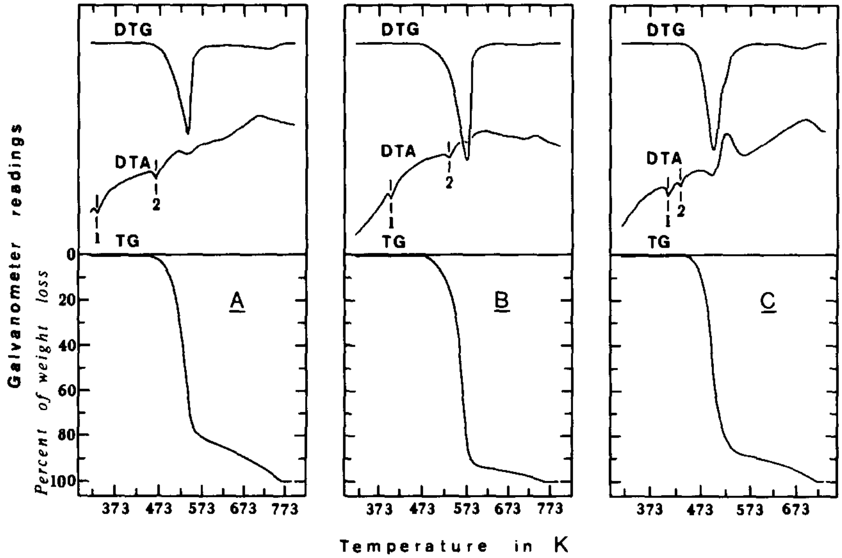

Fig. 1. Dynamic thermal analyses of (A) ethanaminium iodide, (B) *N*-propylpropanaminium iodide and (C) *N*,*N*,*N*-tributylbutanaminium iodide. (1) Solid state phase transition; (2) melting.

TABLE 1

α versus T for the volatilisation of ammonium iodide (A), *N*-propylpropanamonium iodide (B) and *N*,*N*,*N*-tributylbutanaminium iodide (C)

α	Temperature (K)		
	A	B	C
0.10	489.6	519.7	472.0
0.18	502.4	530.9	478.9
0.26	511.2	539.1	484.3
0.34	517.5	544.5	488.3
0.42	522.1	550.1	491.6
0.50	526.4	555.4	495.2
0.58	530.6	559.7	498.4
0.66	534.4	564.0	503.3
0.74	537.7	568.1	509.3
0.82	542.0	–	–
0.90	547.0	–	–

determined from at least three replicate measurements. An example of a measurement is given in Table 1.

RESULTS AND DISCUSSION

General features of the thermal processes

The thermoanalytical curves recorded under both dynamic and quasi-isothermal-isobaric conditions for the few chosen compounds are shown in

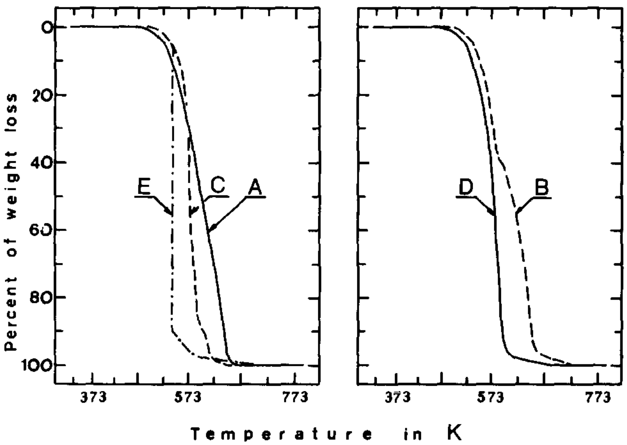

Fig. 2. Quasi-isothermal-isobaric thermogravimetric analyses of (A) ammonium iodide, (B) ethanaminium iodide, (C) *N*-ethylethanaminium iodide, (D) *N*,*N*-diethylethanaminium iodide and (E) *N*,*N*,*N*-triethylethanaminium iodide.

Figs. 1 and 2. To facilitate further discussion the essential parameters characterising the thermal behaviour of the compounds studied, derived from the thermal analysis curves, together with the available literature information are given in Table 2.

All the compounds studied undergo complete volatilisation upon heating up to around 750 K. The thermal processes accompanying volatilisation, are in most cases, complex (see Table 2). This is particularly demonstrated by the pattern of the DTA curves (see, for example, Fig. 1) and also the Q-TG curves (see, for example, Fig. 2). With simple decompositions, a single endothermic effect is expected, as has been observed during volatilisation of chloride and bromide salts of alkanamines [10,12]. The volatilisation of iodide salts is often accompanied by exothermic effects: this implies that side processes proceed simultaneously with the primary decomposition. The thermolyses of chloride, bromide and also hexachlorostannate salts of alkanamines [10–12] are characterised by a simple decomposition pattern, as mentioned above, and also by the fact that at the end of the process a "tail" is seen which we believe is caused by a kinetic phenomenon, namely, the decrease in the volatilisation rate due to non-continuous changes in the geometric surface area of a condensed phase. The thermal decomposition of iodide salts is also sometimes accompanied by a "tail" whose shape, however, indicates the occurrence of side processes such as oxidation or carbonisation. Thermolysis of some of the compounds studied is preceded by solid state phase transitions or melting. The temperatures corresponding to these processes derived in this work compare well with those reported in the literature.

The thermolysis temperatures, namely T_p (from DTG and DTA), $T_{0.01}$, $T_{0.1}$, $T_{0.74}$ and ΔT, are characteristic features for a given compound. For quaternary salts, T_p, $T_{0.01}$, $T_{0.1}$ and $T_{0.74}$ values decrease markedly with increasing length of the *n*-alkyl substituent. A similar tendency is rather weak in the case of hydriodides of primary, secondary and tertiary amines. The characteristic temperatures of thermolysis of iodide salts of alkanamines are, in general, very similar to those reported earlier for the corresponding bromide salts [12]. It is, however, worth mentioning that iodides volatilise at higher temperatures than the corresponding chloride salts [10]. On the other hand, the characteristic temperatures of thermolysis of iodides are lower than those of the corresponding hexachlorostannate salts [11]. These trends correlate qualitatively with the stability of the alkanaminium salts.

The nature of the thermal processes

The hydrogen bond between nitrogen and proton is, undoubtedly, the weakest bonding side in molecules of alkanamine hydriodides. Provided the crystal structure of these compounds is preserved, the hydrogen bond is part of a whole system of interactions which hold together all the fragments in

TABLE 2

The thermal characteristics of the alkanaminium iodides

Compound		Character of the processes [b]	Peak temperature [c] (K)					Temperature [c] (K)			$T_{0.01}$ [d]
No.	Formula [a]		DTG	DTA				$T_{0.1}$	$T_{0.74}$	ΔT	
				T_p		T_σ	T_m				
				Endo	Exo						
1	$[NH_4]I$	R	534	535				489.6	537.7	48.1	445 442 * 501 **
2	$[CH_3NH_3]I$	R	556			419 [e] 414 [8] 415 [17]	544; D [e] 533–543 [23] 536–538; D [24]	514.9	562.5	47.6	472 474 *
3	$[(CH_3)_2NH_2]I$	C	528 740		518 715		431 [e] (423–426) [e] 420 [25] 426 [23] 428 [26]	485.9			432 435 *
4	$[(CH_3)_3NH]I$	C	541		535		533; D [27]	498.3	552.0	53.7	450 447 *
5	$[(CH_3)_4N]I$	R	629	626				585.4	628.7	43.3	552 546 *
6	$[C_2H_5NH_3]I$	C	534 730	530	513 703	333 [e]	468 [e] (458–460) [e] 440 [28] 462 [23]	495.6			439 446 * 501 **
7	$[(C_2H_5)_2NH_2]I$	C	520 703		515 702	309 [e] 373 [e]	448 [e] (443–444) [e] 438 [28] 441–443 [29] 445 [23] 445–447 [30]	489.8			445 442 * 501 **
8	$[(C_2H_5)_3NH]I$	C	535 719		520 719		456 [e] (451–453) [e] 446 [28] 454 [23]	494.7			436 443 * 488 **

9	$[(C_2H_5)_4N]I$	R	561	561		471 ^{e} 465 [32] 467 [33] 476 [23]	563 [34] 575 [35]	544.3	563.8	19.5	519 522 * 503 **
10	$[n\text{-}C_3H_7NH_3]I$	C	532 728		528 728		465 ^{e} (455–459) ^{e}	487.4			436 435 *
11	$[(n\text{-}C_3H_7)_2NH_2]I$	C	571	575	728	390 ^{e}	526 ^{e} (513–518) ^{e} 502 [28] 503–508 [30]	519.7	568.1	48.4	475 472 *
12	$[(n\text{-}C_3H_7)_3NH]I$	C	558 752		549 749		512; D ^{e}	517.4	572.5	55.1	462 462 *
13	$[(n\text{-}C_3H_7)_4N]I$	R	540 556	556		421 ^{e} 418 [32] 419 [36]	543; D^{e} (556–559; D) ^{e} 566 [37] 566–568 [38]	527.5	550.9	23.4	501 495 *
14	$[n\text{-}C_4H_9NH_3]I$	C	533 734	544	523 716		447 ^{e} (440–443) ^{e}	483.3			416 428 *
15	$[(n\text{-}C_4H_9)_2NH_2]I$	C	571	574	750		546; D ^{e} (530–533; D) ^{e}	528.7	578.7	50.0	484 480 *
16	$[(n\text{-}C_4H_9)_3NH]I$	C	559 739		551 740		388 ^{e} (370–372) ^{e} 374–375 [39] 376 [40]	495.1	568.5	73.4	435 433 *
17	$[(n\text{-}C_4H_9)_4N]I$	C	498 703	493	521 710	401 ^{e} 392 [32,36]	426 ^{e} (415–417) ^{e} 417–418 [35] 418 [32] 419 [36,41] 421 [42]	472.0	509.3	37.3	444 433 *

---

[a] For chemical names of amines see ref. 10.

[b] R, Regular; C, complex.

[c] The symbols were taken from ref. 22: T_p, temperature of the peak; T_σ, temperature of the solid-state phase transition; T_m, temperature of melting; T_α, temperature at which the extent of the process is equal to α; $\Delta T = T_{0.74} - T_{0.1}$.

[d] Temperature of the onset of volatilisation: without asterisk, derived from dynamic thermal analysis curves; with one asterisk (*), determined from eqn. (2); with two asterisks (**), derived from quasi-isothermal-isobaric thermogravimetric curves.

[e] From this work. The values in parentheses are the melting points determined by a standard capillary method. D, Decomposition.

the lattice. With heating, however, this bond can be expected to rupture. Thus, the primary process in the thermolysis of alkanamine hydriodides is the release of the appropriate amines and HI. The prediction regarding the primary step in the thermolysis of quaternary salts is not so simple. This is because all the N–C bonds in tetrahedral alkanaminium cations are non-distinguishable and have a much higher energy than the N · · · H hydrogen bond in primary, secondary or tertiary alkanaminium cations. Experiments regarding the decomposition of quaternary alkanaminium halides [10,12,43] suggest that the primary step in the thermal decomposition of these derivatives is release of the appropriate haloalkanes and tertiary amines in the gaseous phase. This theory is supported by the fact that the reverse process proceeds relatively easily [44]. In conclusion, the primary step in the thermolysis of the compounds studied can be summarised with the equation

$$[R_pNH_{4-p}]I(l,c) \rightarrow R_{p-a}NH_{3-p+a}(g) + (1-a)HI(g) + aRI(g) \qquad (1)$$

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

The volatilisation temperatures for alkanaminium iodides (Table 2) are far above the boiling points of the corresponding amines and HI [15]. Therefore, in all cases one can expect release of the decomposition fragments in the gaseous phase. Several experimental and theoretical works indicate, however, the possible existence of weak interactions between molecules of amines or amines and HI after leaving the condensed phase [4,5,9,45–47]. Such interactions are expected to be rather weak especially at the relatively high temperatures of the volatilisation process. One, therefore, may assume that eqn. (1), which takes into account the fact that dissociation fragments behave as kinetically free molecules in the gaseous phase, is a valid expression of the primary step in the thermal decomposition of the compounds examined. This assumption forms a convenient framework for further thermochemical and kinetic considerations.

The nature of the secondary and side processes indicated by the thermoanalytical curves has not been studied. As mentioned above, it may be thought that secondary processes are of oxidative origin and that they occur due to the expected presence of I_2 molecules in the reacting system. This latter species may easily occur because HI is thermodynamically unstable ($\Delta G^{\ominus}_{f,298} = 1.7$ kJ mol^{-1} [14]). This implies that the compound can spontaneously decompose into its constituent elements. This does not actually occur at ambient temperature as the process presumably requires that an activation barrier be overcome; this should be easy at the higher temperatures of the volatilisation process. A possible side process would be the destruction of the organic parts of the molecules. All secondary and side processes are usually observed when dissociation and volatilisation are far advanced. Moreover, they most probably occur with the participation of gaseous reactants, and thus do not affect the thermogravimetric curves.

Therefore, it seems justifiable to use dynamic TG curves for the examination of the thermodynamics and kinetics of reaction (1).

Thermodynamics and kinetics of the thermal dissociation

Reaction (1) presents a simple chemical process which expresses the release of two gaseous molecules from one structural unit of alkanaminium iodide. If the reacting system attains the equilibrium state at a certain temperature then the experimental extent of the decomposition (α) is directly related to the pressures of both gaseous components and, thus, to the equilibrium constant. This allows the evaluation of the enthalpy change for the process from the van't Hoff equation which can be written in the form

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

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 volatilisation temperature, i.e. the temperature at which P reaches P_0. This approach implies that the process does not need to overcome any additional energy barrier apart from that resulting from the thermodynamic requirements. In addition, other processes, such as diffusion of gaseous products, heat transfer, side reactions, etc., cannot influence the decomposition process.

Using experimental α versus T dependencies the ΔH_v and T_v values were derived and these are listed in Table 3. For two of the compounds studied, the dissociation pressures were measured by other methods. The reported literature values of ΔH_v and T_v or their values evaluated on the basis of literature P versus T dependencies and eqn. (2), are also shown in Table 3. As can be seen, the ΔH_v, for NH_4I derived in this work compares well with literature values. On the other hand, the T_v values evaluated for this compound from literature P versus T dependencies are more than 100 K higher than values found in the present study. Also, when thermal analyses were performed on a similar instrument but using samples of a larger mass placed in different crucibles, the temperatures corresponding to the decomposition of NH_4I were around 70 K higher than those shown in Table 2 [48]. All the above clearly indicates that the T_v values are markedly dependent on the conditions under which the process takes place. The discrepancies between the ΔH_v and T_v values derived in this work for $[Me_4N]I$ and those evaluated from the P versus T data reported by Smith and Calvert [43] are the result of the existence of a kinetic barrier for the process. This problem will be discussed subsequently.

The dissociative volatilisation of alkanaminium iodides presents an example of a simple process proceeding in the condensed phase. For such a process the classical Arrhenius model can be applied to describe the kinetic

TABLE 3

Thermodynamic and kinetic constants for the volatilisation of alkanaminium iodides

Compound No.	Thermodynamic constants [a]		Kinetic constants [c]				Range of α [d]
			$g(1-\alpha)=\alpha$ (R1)		$g(1-\alpha)=\alpha-(1-\alpha)^{1/2}$ (R2)		
	ΔH_v (kJ mol^{-1})	T_v (K)	E_a (kJ mol^{-1})	Z (s^{-1})	E_a (kJ mol^{-1})	Z (s^{-1})	
1	175	547	167	1.5×10^4	196	2.7×10^5	0.10–0.90
	159 [49] [b]	675 [49] [b]					
		677 [50]					
	182 [51]						
	184 [52]						
	185 [46]						
	189 [43] [b]	678 [43] [b]					
	193 [43] [b]	676 [53] [b]					
2	212	572	203	3.0×10^5	231	4.1×10^6	0.10–0.82
3	156	552	148	1.4×10^3	165	5.5×10^3	0.10–0.66
4	172	558	163	7.5×10^3	185	5.0×10^4	0.10–0.74
5	(275)	(635)	265	1.1×10^7	311	6.2×10^8	0.10–0.90
	170 [43] [b]	579 [43] [b]					
6	171	557	162	6.5×10^3	176	1.7×10^4	0.10–0.50
7	176	548	167	1.6×10^4	181	4.5×10^4	0.10–0.50
8	164	559	156	3.0×10^3	169	7.5×10^3	0.10–0.50
9	(502)	(567)	493	7.9×10^{18}	580	5.9×10^{22}	0.10–0.90
10	157	552	149	1.7×10^3	165	6.7×10^3	0.10–0.66
11	202	574	193	1.0×10^5	219	9.3×10^5	0.10–0.74
12	177	578	168	6.0×10^3	190	4.1×10^4	0.10–0.74
13	(357)	(554)	348	4.1×10^{12}	415	4.1×10^{15}	0.10–0.90
14	146	552	138	5.5×10^2	153	1.9×10^3	0.10–0.66
15	207	584	198	1.1×10^5	224	1.0×10^6	0.10–0.74
16	133	576	124	6.7×10	141	2.5×10^2	0.10–0.74
17	(218)	(511)	210	8.9×10^6	239	1.7×10^8	0.10–0.74

[a] The values of ΔH_v and T_v were evaluated using eqn. (2) and a standard least-squares procedure. Values in parentheses are for quaternary salts.

[b] Values determined using eqn. (2) and literature P versus T dependencies.

[c] The kinetic constants were determined from the equation: $g(1-\alpha)=(ZT/\phi)[\exp(-E_a/2RT)]$. This equation was rearranged into: $\ln[g(1-\alpha)/T]$ versus $1/T$ and values of E_a and Z were derived by using a standard least-squares procedure.

[d] The thermal dissociation range over which α versus T data points were drawn from TG curves.

phenomena. This approach requires that only one step in the overall process is a slow one and that this rate-determining step governs the kinetics of the whole reaction. According to this approach the integral kinetic equation takes the form

$$g(1-\alpha) = (ZT/\phi)\exp(-E_a/2RT) \tag{3}$$

which is adequate for linear temperature-increase conditions [54]. 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, E_a represents the activation barrier for the reaction and the factor 2 in the exponential term accounts for the fact that the transition state for the dissociative volatilisation of alkanaminium iodides is considered as a loosely bound complex of amine and HI (or RI) molecules [11,12,55].

Using experimental α versus T dependencies the kinetic constants were derived from eqn. (3) choosing two reaction models, namely the zero kinetic order model (R1) and the surface contracting area model (R2) [21]: these are presented in Table 3. These two models were chosen as they seemed to correspond best to the nature of the process and the conditions of its realisation. It was also found that both models fit the experimental data points very well.

A further question arises as to whether this approach provides real information on the kinetics of the processes examined: it is difficult to answer this question, particularly with regard to the reaction pathway. The Arrhenius model presents a somewhat purely formal approach to the kinetics of processes involving solids. Nevertheless, the calculations performed do show that the experimental extent of reaction versus T data points fit the exponential-type dependence resulting from this model. Therefore, some meaning can be ascribed to the activation barrier. For the two chosen reaction models, the E_a values are either somewhat lower than ΔH_v, for the R1 model, or slightly higher than ΔH_v, for the R2 model. If either model actually describes the kinetic phenomena, this would mean that the volatilisation process of all the hydriodides studied proceeds without any additional activation barrier apart from that resulting from the enthalpy change.

Examining both thermodynamic and kinetic data shown in Table 3, it can be seen that the ΔH_v and E_a values for quaternary salts are surprisingly high in comparison with values for other compounds studied. This may suggest that decomposition of these latter derivatives involves a considerable activation barrier.

Thermochemical characteristics

Using the values of ΔH_v derived in this work and certain literature information, several thermochemical characteristics for the compounds examined can be determined on the basis of Hess's law. The various relations

TABLE 4

The thermochemical characteristics (kJ mol^{-1}) of the alkanaminium iodides at 298 K [a]

Compound	$\Delta H_v^\ominus$	$\Delta H_{f,c}^\ominus$		$U^\ominus$		
		This work	From the literature	This work [b]		From the literature
				A	B	
$[NH_4]I$	182 (182)	−202 (−202)	−201.4 [14,16] −202.1 [58,59]	631	631	594 [63] 603 [64] 609 [65] 619, 621 [66] 628 [16] 634 [67] 637 [58]
$[MeNH_3]I$	232 (183)	−228 (−179)	−200.5 [60] −200.7 [16]	632	583	608 [16]
$[Me_2NH_2]I$	178 (196)	−171 (−188)	−200.0 [60] −201.7 [16]	554	571	587 [16]
$[Me_3NH]I$	179 (186)	−177 (−185)	−202.7 [60] −203.0 [16]	539	547	565 [16]
$[Me_4N]I$	(181)	(−190)	−203.5 [16] −203.9 [61]		531	477 [68] 498 [69] 506 [61] 518 [70] 544 [16]
$[EtNH_3]I$	192 (193)	−214 (−214)	−234.1 [18]	581	581	608, 640 [18]
$[Et_2NH_2]I$	195 (204)	−242 (−250)	−263.0 [18]	552	560	580, 624 [18]
$[Et_3NH]I$	179 (219)	−246 (−285)	−289.0 [18]	510	549	558, 601 [18]
$[Et_4N]I$	(216)	(−316)	−300.2 [61] −317.0 [18] −331.5 [62]		530	396 [62] 448 [68] 449 [69] 459 [70] 478 [61] 583 [18]
$[n\text{-}PrNH_3]I$	174 (198)	−218 (−241)		557	580	
$[n\text{-}Pr_2NH_2]I$	217 (206)	−307 (−295)		565	554	
$[n\text{-}Pr_3NH]I$	188 (211)	−323 (−345)		509	531	
$[n\text{-}Pr_4N]I$	(204)	(−395)			505	
$[n\text{-}BuNH_3]I$	159 (203)	−225 (−268)		540	583	
$[n\text{-}Bu_2NH_2]I$	220 (220)	−351 (−350)		564	563	

Table 4 (continued)

Compound	$\Delta H_v^\ominus$	$\Delta H_{f,c}^\ominus$		$U^\ominus$		
		This work	From the literature	This work [b]		From the literature
				A	B	
[n-Bu_3NH]I	148 (182)	−344 (−377)		464	497	
[n-Bu_4N]I	(185)	(−460)			484	

[a] Values estimated are given in parentheses.

[b] A, values determined from the thermochemical cycle; B, values evaluated from the Kapustinskii–Yatsimirskii equation (using $r_{I^-} = 0.22$ nm [13,71] and modifying values of r_K from ref. 57 relative to $r_{Cl^-} = 0.181$ [10,13,56,71]).

between the thermochemical quantities can be conveniently presented in the form of a thermochemical cycle. Such a cycle for the alkanaminium iodides would be analogous to that for the chloride salts which has been published elsewhere [56]. The relations resulting from the thermochemical cycle for hydriodides of alkanamines are presented below in eqns. (4) and (5)

$$\Delta H_{f,c}^\ominus\left[(R_pNH_{4-p})I\right] = \Delta H_{f,g}^\ominus\left[R_pNH_{3-p}\right] + \Delta H_{f,g}^\ominus[HI] - \Delta H_v^\ominus \qquad (4)$$

$$U^\ominus\left[(R_pNH_{4-p})I\right] = \Delta H_{f,g}^\ominus\left[R_pNH_{4-p}^+\right] + \Delta H_{f,g}^\ominus[I^-] - \Delta H_{f,c}^\ominus\left[(R_pNH_{4-p})I\right] - 2RT \qquad (5)$$

All magnitudes in eqns. (4) and (5) refer to 298 K and 1 atm, $\Delta H_f^\ominus$ denotes the enthalpy of formation of a given species ($p = 1$–3) and $(U^\ominus + 2RT)$ is the lattice enthalpy ($U^\ominus$ represents the lattice energy).

The enthalpies of volatilisation of hydriodides derived from eqn. (2) do not refer to 298 K. Therefore, they were modified according to the equation

$$\Delta H_v^\ominus = \Delta H_v + \Sigma\Delta H_\sigma^\ominus + \Delta H_{fn}^\ominus - \int_{298}^{T} \Delta C_p^\ominus \, dT \qquad (6)$$

where the term $\Sigma\Delta H_\sigma^\ominus$ arises from any polymorphic transitions which these compounds may undergo between 298 K and the onset of fusion or volatilisation, $\Delta H_{fn}^\ominus$ is the enthalpy of fusion, while the term $\int_{298}^{T} \Delta C_p^\ominus \, dT$ accounts for the change in enthalpy resulting from changes in the heat capacities of the reactants. The enthalpies of solid-state transitions and fusion were either taken directly from the literature [8,17] or were estimated in the previously described manner [12]. In the absence of heat capacity data for salts and the corresponding decomposition products, a value of −7.0 kJ mol^{-1} was arbitrarily chosen for the heat capacity term in eqn. (6). This value was assumed on the basis of our previous work regarding the thermochemistry of hydrochloride and hydrobromide salts of alkanamines [10,12]. The modified $\Delta H_v^\ominus$ values are listed in Table 4.

To evaluate the thermochemical quantities derived from eqns. (4) and (5), we used the values of the enthalpies of formation of the gaseous amines and corresponding alkanaminium cations from ref. 57. Furthermore, the $\Delta H^{\ominus}_{f,g}$[HI] and $\Delta H^{\ominus}_{f,g}[I^-]$ values were assumed to be (kJ mol^{-1}) 26.5 [14] and −196 [13–15], respectively. The $\Delta H^{\ominus}_{f,c}$ and $U^{\ominus}$ values derived for the hydriodides of ammonia and the primary, secondary and tertiary amines studied, together with the available literature data, are shown in Table 4.

The values in Table 4 demonstrate that the standard enthalpies of formation and the crystal lattice energies derived from the thermochemical cycle both decrease with an increase in the size and number of alkyl substituents (p) at the nitrogen atom. For previously examined chloride [10], bromide [12] and hexachlorostannate [11] salts of alkanamines, the analogous dependencies are almost linear, indicating the additive nature of both quantities. These dependencies enabled the estimation, by extrapolation, of $\Delta H^{\ominus}_{f,c}$ and $U^{\ominus}$ values for the corresponding quaternary salts. In the case of the compounds studied, the values of $\Delta H^{\ominus}_{f,c}$ and $U^{\ominus}$ versus P are poorly approximated by linear relationships. It does not, therefore, seem appropriate to use the above mentioned procedure for the estimation of the thermochemical characteristics of quaternary iodide salts.

In addition, with respect to the thermochemistry of the compounds examined, the approximate method was used to evaluate the crystal lattice energies. This method was originally developed and subsequently improved by Kapustinskii [72] and Yatsimirskii [73]. According to these authors, the lattice energy of ionic crystals can be approximated by using the equation

$$U = 120.2[(\Sigma_n)Z_K Z_A/(r_K + r_A)][1 - 0.0345/(r_K + r_A) + 0.087(r_K + r_A)] \quad (\text{kJ mol}^{-1}) \qquad (7)$$

where (Σ_n) 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, using available literature information (see footnotes of Table 4), are listed in Table 4. A further insight into the thermochemistry of the compounds examined was made possible by calculating $\Delta H^{\ominus}_{f,c}$ and $\Delta H^{\ominus}_{v}$ values from rearranged forms of eqns. (4) and (5). For this estimation, the ancillary data mentioned above were used. This enabled the thermochemical characteristics of the hydriodides of amines to be obtained. The enthalpies of formation and the enthalpies of the thermal decomposition for quaternary salts were similarly estimated by using U values evaluated from the Kapustinskii–Yatsimirskii equation and values of the enthalpies of formation of the corresponding quaternary alkanaminium cations from ref. 57. In the latter, the calculation values of $\Delta H^{\ominus}_{f,g}$[MeI], $\Delta H^{\ominus}_{f,g}$[EtI] and $\Delta H^{\ominus}_{f,g}$[n-PrI] were taken to be 14.7, −7.5 and −30.3 kJ mol^{-1}, respectively [60]. The value of $\Delta H^{\ominus}_{f,g}$[n-BuI] was estimated to be

-52.8 kJ mol^{-1} by Benson's group additivity method [74]. The $\Delta H_{f,c}^{\ominus}$ and $\Delta H_v^{\ominus}$ values evaluated in the manner described above for all the compounds examined are shown, in parentheses, in Table 4.

For ammonium iodide only, the thermochemical characteristics evaluated in both ways agree very well with each other. They also fit well with the reported literature values. For ethanaminium iodide, *N*-ethylethanaminium iodide, *N*-propylpropanaminium iodide and *N*-butylbutanaminium iodide, the agreement between the values derived from the thermochemical cycle and the estimated values is also very good, although they do not correspond well with the available literature values. For methanaminium iodide, the values estimated from the thermochemical cycle do not fit either those estimated from eqn. (7) or those reported in the literature. It is perhaps worth mentioning that the $\Delta H_v^{\ominus}$ value for $[MeNH_3]I$ is much higher than that predicted from eqn. (7). For the remaining compounds the crystal lattice energies estimated from eqn. (7) are higher than those resulting from the thermochemical cycle. This is because $\Delta H_v^{\ominus}$ values derived from dynamic thermogravimetric measurements are generally lower than those predicted on the basis of eqn. (7) (see values in parentheses in Table 4). These discrepancies are most probably a consequence of the occurrence of side processes. In such cases, the TG curves correspond to the overall complex process rather than to the simple decomposition process given in reaction (1). Special attention has to be paid to the quaternary salts. The predicted enthalpy changes for the decomposition process correspond very well to other $\Delta H_v^{\ominus}$ values for a given group of compounds (Table 4). On the other hand, these predicted values are markedly lower than those determined using thermogravimetric curves (Table 3). The most probable explanation of this is that the thermal decomposition of the quaternary salts involves a considerable activation barrier in addition to that resulting from the thermodynamic requirements, i.e. $\Delta H_v^{\ominus}$. The enormously high $\Delta H_v^{\ominus}$ value for $[MeNH_3]I$ (Table 3) is most probably also due to the existence of some kinetic barrier for the decomposition process.

CONCLUDING REMARKS

The thermolysis of alkanaminium iodides is complex compared with the thermal dissociation of the chloride and bromide salts of the corresponding amines. We believe that this is caused by the thermal instability of HI which is expected to be one of the primary decomposition products. The thermochemical characteristics always correspond to a well-defined chemical process or to the state of the system. In our case, this is not always the case and, therefore, the $\Delta H_v^{\ominus}$, $\Delta H_{f,c}^{\ominus}$ and $U^{\ominus}$ values derived cannot be accepted without reservation. Nevertheless, the results of this study follow the general trends observed in the examination of other alkanamine salts [10–12]. They also seem to confirm that the fundamental thermochemical characteristics for alkanaminium halides, such as enthalpies of formation, crystal lattice energies and also "thermochemical" radii, are additive in nature.

Special attention should be devoted to the crystal lattice energy values which express the magnitude of the cohesive forces keeping the constituents in the lattice. Despite the approximate character of the *U* values derived in this work (Table 4), it can be seen that they vary rather insignificantly with the size and number of alkyl substituents at nitrogen atom. This would mean that the cohesive forces, defined by crystal lattice energy, are similar in all the compounds studied. To explain this phenomenon, it should be remembered that the major contribution to the lattice energy of ionic substances is from electrostatic interactions between the charged centres [75,76]. In alkanaminium iodides the centre of the negative charge is located on the iodine atom. It is not known a priori where the positive charge centre is located. If it is close to the nitrogen atom, then the N–I distance would predominantly influence the energy of the electrostatic interactions and, thus, the crystal lattice energy. From the crystallographic data for hydriodides of *N,N*-dimethylmethanamine and *N,N*-diethylethanamine, the $>$N–H $\cdots$ I distance only varies from 0.346 to 0.360 nm, respectively [6,77]. Therefore one could expect similar *U* values for both the latter compounds. The qualitative agreement with this prediction can be seen in the data of Table 4. This simple explanation could be substantiated by calculating the electrostatic part of the crystal lattice energy from the known crystal structures of iodide salts of nitrogen organic bases. We are currently working on this problem.

ACKNOWLEDGEMENT

We would like to thank Mrs. I. Nikel for experimental assistance.

REFERENCES

1 P. Dokurno, J. Łubkowski and J. Błażejowski, J. Therm. Anal., in press.
2 E. Moreno-Gonzales, M. Marrand and J. Neel, J. Chim. Phys. Phys. Chim. Biol., 74 (1977) 563.
3 O. Knop, I.A. Oxton and M. Falk, Can. J. Chem., 57 (1979) 404.
4 P. Kollman, A. Dearing and E. Kochanski, J. Phys. Chem., 86 (1982) 1607.
5 A. Brciz, A. Karpfen, H. Lischka and P. Schuster, Chem. Phys., 89 (1984) 337.
6 M.A. James, T.S. Cameron, O. Knop, M. Neuman and M. Falk, Can. J. Chem., 63 (1985) 1750.
7 M. Eckert and G. Zundel, J. Phys. Chem., 91 (1987) 5170.
8 H. Ishida, R. Ikeda and D. Nakamura, Bull. Chem. Soc. Jpn., 59 (1986) 915.
9 J.T. Cheung, D.A. Dixon and D.R. Herschbach, J. Phys. Chem., 92 (1988) 2536.

10 J. Błażejowski and E. Kowalewska, Thermochim. Acta, 105 (1986) 257.
11 T. Janiak and J. Błażejowski, Thermochim. Acta, 141 (1989) 93.
12 J. Łubkowski and J. Błażejowski, Thermochim. Acta, 157 (1990) 259.
13 K.P. Mishchenko and A.A. Ravdel, Kratki Spravochnik Fiziko, Khimicheskikh Velichin, Khimiya, Leningrad, 5th edn., 1967.
14 D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney and R.L. Nuttall, J. Phys. Chem. Ref. Data, 11 (1982) Suppl. 2.
15 Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 67th edn., 1987–1988.
16 J.W. Wilson, J. Chem. Soc., Dalton Trans., (1976) 890.
17 O. Yamamuro, M. Oguni, T. Matsuo and H. Suga, Thermochim. Acta, 98 (1986) 327.
18 B.M. Derekhshan, A. Finch, P.N. Gates and M. Stephens, J. Chem. Soc., Dalton Trans., (1984) 601.
19 J. Paulik, F. Paulik and L. Erdey, Anal. Chim. Acta, 34 (1966) 419.
20 J. Paulik and F. Paulik, Comprehensive Analytical Chemistry, Vol. 12, Part A, Elsevier, Amsterdam, 1981, p. 47.
21 J. Błażejowski, J. Szychlinski and K. Windorpska, Thermochim. Acta, 46 (1981) 147.
22 R.C. Mackenzie, J. Therm. Anal., 21 (1981) 173.
23 L. Wagner, Z. Kristallogr. Mineral., 43 (1907) 148.
24 H. Blitz and F. Max, Justus Liebig's Ann. Chem., 423 (1921) 300.
25 F. Kaufler and E. Kunz, Chem. Ber., 42 (1909) 2482.
26 R. Willstatter and T. Wirth, Chem. Ber., 42 (1909) 1908.
27 Beilsteins Handbuch der Organischen Chemie, Springer, Berlin, 4th edn., 1922, p. 47.
28 W.M. Dehn, J. Am. Chem. Soc., 34 (1912) 290.
29 B. Flurscheim, J. Prakt. Chem., 68 (1903) 345.
30 W. Steinkopf and R. Bessaritsch, J. Prakt. Chem., 109 (1925) 230.
31 J. Radomski, Fiz. Dielektr. Radiospektrosk., 13 (1986) 253.
32 J. Levkov, W. Kohr and R.A. Mackay, J. Phys. Chem., 75 (1971) 2066.
33 B. Szafranska and Z. Pajak, J. Mol. Struct., 99 (1983) 147.
34 W. Oswald and H. Roederer, Koll. Z., 82 (1938) 174.
35 P.A.S. Smith and S. Frank, J. Am. Chem. Soc., 74 (1952) 509.
36 T.G. Coker, J. Ambrose and G.J. Janz, J. Am. Chem. Soc., 92 (1970) 5293.
37 M.J. McDowell and C.A. Kraus, J. Am. Chem. Soc., 73 (1951) 3293.
38 H.M. Daggett, E.J. Blair and C.A. Kraus, J. Am. Chem. Soc., 73 (1951) 799.
39 H.S. Young and C.A. Kraus, J. Am. Chem. Soc., 73 (1951) 4732.
40 C.R. Witschonke and C.A. Kraus, J. Am. Chem. Soc., 69 (1947) 2472.
41 M.B. Reynolds and C.A. Kraus, J. Am. Chem. Soc., 70 (1948) 1709.
42 A.A. Vernon, W.F. Luder and M.Giella, J. Am. Chem. Soc., 63 (1941) 862.
43 A. Smith and R.P. Calvert, J. Am. Chem. Soc., 26 (1914) 1363.
44 F.A. Petrachkov, Zh. Fiz. Khim., 28 (1954) 1408.
45 J.D. Lambert and E.D.T. Strong, Proc. Roy. Soc. (London), Ser. A, 200 (1950) 566.
46 C.G. de Kruif, J. Chem. Phys., 77 (1982) 6247.
47 N.S. Golubev and G.S. Denisov, Khim. Fiz., (1982) 563.
48 L. Erdey, S. Gal and G. Liptay, Talanta, 11 (1964) 913.
49 F.M.G. Johnson, Z. Phys. Chem., 65 (1909) 36.
50 M.M. Markowitz and D.A. Boryta, J. Phys. Chem., 66 (1962) 1477.
51 N.W. Luft, Ind. Chem., 31 (1955) 502.
52 R.H. Purcell and W. de Lange, J. Chem. Soc., (1929) 275.
53 A. Smith and R.H. Lombard, J. Am. Chem. Soc., 37 (1915) 38.
54 J. Błażejowski, Thermochim. Acta, 76 (1984) 359.
55 D.J. Meshi and A.W. Searcy, High Temp. Sci., 6 (1974) 221.
56 J. Błażejowski, Thermochim. Acta, 68 (1983) 233.
57 J. Błażejowski, J. Szychlinski and E. Kowalewska, Thermochim. Acta, 108 (1986) 239.

58 H.D.B. Jenkins and D.F.C. Morris, Mol. Phys., 32 (1976) 231.
59 Landoldt–Bornstein, Zahlenwerte und Funktionen, Band II, Teil 4, Springer-Verlag, Berlin, 1961.
60 J.B. Pedley, R.D. Naylor and S.P. Kirby, Thermochemical Data of Organic Compounds, Chapman and Hall, London, 2nd edn., 1986.
61 Y. Nagano, M. Sakiyama, T. Fujiwara and Y. Kondo, J. Phys. Chem., 92 (1988) 5823.
62 S.I. Nwankwo, Thermochim. Acta, 47 (1981) 157.
63 M.F.C. Ladd and W.H. Lee, J. Inorg. Nucl. Chem., 13 (1960) 218.
64 H. Grimm, Handb. Phys., 24 (1927) 518.
65 W.E. Bleick, J. Chem. Phys., 2 (1934) 160.
66 M.N. Sharma and M.P. Madan, Indian J. Phys., 38 (1964) 305.
67 A.L. Goodlife, H.D.B. Jenkins, S.V. Martin and T.C. Waddington, Mol. Phys., 21 (1972) 761.
68 M.F.C. Ladd, Z. Phys. Chem. NF, 72 (1970) 91.
69 D.A. Johnson and J.F. Martin, J. Chem. Soc., Dalton Trans., (1973) 1585.
70 R.H. Boyd, J. Chem. Phys., 51 (1969) 1470.
71 K.B. Yatsimirskii, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk, (1948) 398.
72 A.F. Kapustinskii, Quart. Rev. (London), 10 (1956) 283.
73 K.B. Yatsimirskii, Zh. Neorg. Khim., 6 (1961) 518.
74 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haugen, H.E.O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.
75 Ch. Satyanarayana, Phys. Rev. B, 30 (1984) 1004.
76 G. Raghurama and R. Narayan, J. Phys. Chem. Solids, 44 (1983) 633.
77 G.M. Sheldrick and W.S. Sheldrick, Acta Crystallogr. Sect. B, 26 (1970) 1334.