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THERMAL PROPERTIES OF AMINE HYDROCHLORIDES. PART II. THERMOLYSIS AND THERMOCHEMISTRY OF ALKANAMINIUM CHLORIDES *

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ABSTRACT

Thermoanalytical methods (DTA, TG, and DTG) have been applied to the investigation of the thermal properties of unbranched compounds of general formula $[(C_nH_{2n+1})_p NH_{4-p}]Cl$, with $n = 1$–4 and $p = 2$–4, and several other cyclic and open chain branched aliphalic alkanaminium chlorides. Thermal decomposition of all the compounds studied occurs in one step and leads to their total volatilization. The experimental TG curves were used for the examination of the thermodynamics and kinetics of this process. The nature of the thermal decomposition of the salts is also considered.

The enthalpies of the thermal dissociation were evaluated on the basis of the Van't Hoff equation. Thus derived values together with the available literature data were used for the estimation of the enthalpy of formation and the energy of the crystal lattice of the salts. Furthermore, this information was used for the evaluation of the enthalpy of formation of quaternary alkanaminium ions and alkane cation affinities. The "thermochemical" radii for alkanaminium ions were also derived from the Kapustinskii–Yatsimirskii equation.

The Jacobs and Russell-Jones approach was applied for the description of the kinetics of volatilization of amine hydrochlorides. It was found that this model approximates very well with the experimental TG data and evaluated values of the activation energy are very close to the values of the enthalpy for the process. Moreover, this approach accounts also for the limitation of the volatilization rate at the end of the process as a result of a decrease of the geometric surface area of a condensed phase. On the other hand, the application of the standard methods in the case of quaternary salts did not explain the basic questions regarding the kinetics and mechanism of the thermal decomposition of this group of compounds.

The values of parameters characterizing thermal properties of alkanaminium chlorides, namely, temperatures of the thermal effects, as well as thermochemical and kinetic constants of thermolysis depend notably on the number of alkyl substituents and the length and structure of an alkyl group. The influence of the length and number of *n*-alkyl substituents on the values of both the enthalpy of formation and the crystal lattice energy is thoroughly discussed. The essential thermal and thermochemical characteristics for alkanaminium chlorides have been also reviewed.

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INTRODUCTION

The chloride salts of aliphatic amines are one of the simplest ionic derivatives of organic compounds. They are formed upon interaction of amines with hydrogen chloride or chloroalkanes in condensed phases [2,3]. Many of these compounds have been known for a long time, and a number of their properties have been examined in the past. None the less, the nature of interactions which cause the formation of these derivatives is still not perfectly explained despite considerable theoretical [4–6] and experimental [7–9] efforts which have been undertaken quite recently. In the previous work, devoted to the thermochemistry of primary 1-alkanaminium chlorides [10], we proved that an important source of information is thermoanalytical investigations. The present work is a continuation of this study and its primary objectives are to reveal general features governing the thermal decomposition of alkanaminium chlorides and to establish general regularities between the structure of amine and thermochemistry and thermal properties of appropriate alkanaminium chloride salts. There were also other reasons for undertaking such a study. The examination of the thermal dissociation of mono-1-alkanaminium chlorides [10], hexachlorostannates [11], and hydrochlorides of aromatic bases [12] revealed that the non-isothermal kinetics of the process differ significantly from those characteristic of typical chemical reactions. Extending the study we expected to gather more information regarding this phenomenon. Further, owing to the relatively high proton [13,14] and alkane cation [13,15] affinities of amines the appropriate amminium chlorides exist, in condensed phases, in the form of ion pairs in which the positive charge is gathered predominantly on the nitrogen atom. Therefore, this study should also provide information on the behaviour of highly unsymmetrical ions. Lastly, since alkanaminium chlorides are often used in organic synthesis, as catalysts, as solvents (in liquid state), etc., knowledge of their thermochemistry and thermal properties has also a considerable practical importance.

EXPERIMENTAL

All reagents used were the best available grades. The amine hydrochlorides were synthesized as previously described [10]. Quaternary alkanaminium chlorides were purified by literature methods [16,17]. The purity of the compounds was checked by elementary analysis.

The thermal analyses were carried out on an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference, in a dynamic atmosphere of N_2. The samples weighing 50 mg were placed on one platinum plate [18] (Appendix 1, No. 4). Other operating conditions were: heating rate = ca. 5 K min^{-1}

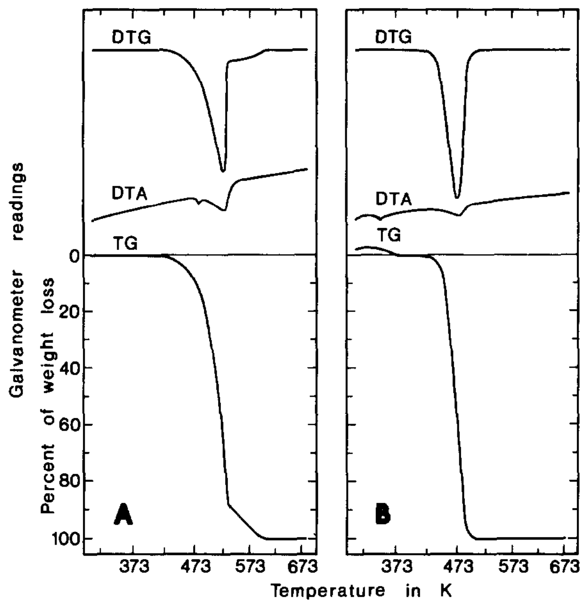

Fig. 1. Thermal analyses of cyclohexanaminium chloride (A) and *N*,*N*,*N*-tributyl-1-butanaminium chloride (B).

and sensitivities of DTG, DTA, and TG galvanometers = 1/10, 1/5 or 1/3, and 50 mg, respectively. All the compounds studied, especially tertiary and quaternary salts, are hygroscopic. To avoid the presence of water the samples, ground in an agate mortar before weighing (if possible), were placed in a sample holder and heated 2 h in vacuo (in a vacuum pistol), prior to analysis, at temperatures below the onset of volatilization.

From the thermogravimetric curves, such as those shown in Fig. 1, the numerical values of the temperature (T) corresponding to certain values of the extent of reaction (α) can be derived [19]. For each compound investigated the set of α vs. T data points was determined from at least three replicate measurements. An example is given in Table 1.

TABLE 1

α versus T dependency for the thermal dissociation of cyclohexanaminium chloride (A) and *N*,*N*,*N*-tributyl-1-butanaminium chloride (B)

T (K)	α									
	0.10	0.18	0.26	0.34	0.42	0.50	0.58	0.66	0.74	0.82
A	473.6	486.6	494.5	501.0	506.9	510.9	515.0	518.5	521.4	525.7
B	451.2	456.7	460.4	463.9	466.8	469.1	471.6	474.1	476.7	479.6

TABLE 2

Thermal characteristics for alkanaminium chlorides

Substance [a]		Peak temperature [b] (K)						Temperature [b] (K)			Parameters of the onset of the second stage	
No.	Formula	DTG	DTA					$T_{0.1}$	$T_{0.82}$	ΔT_α		
			T_σ		T_m		T_p				α	T (K)
			This work	From literature	This work	From literature						
1	$[(CH_3)_2NH_2]Cl$	525	320	313 [21–23]	446	439–442 [24] 439.7 [25] 440 [22,26,27] 442–443 [28] 443–444 [29] 443.6 [30] 444 [21,23,30]	527	467.5	524.9	57.4	0.89	529
2	$[(CH_3)_3NH]Cl$	485	315	308 [21,23,31]		544–545 [32] 544–548 [30] 546–548 [26] 548 [21] 550–551 [30] 553 [33] 553–555 [34] 554–556 [35]	487	438.6	492.0	53.4	0.90	499
3	$[(CH_3)_4N]Cl$	600	405 537	400 [36] 418 [37] 536 [21]		693 [38]	590	572.1	606.5	34.4		
4	$[(C_2H_5)_2NH_2]Cl$	511				488 [39] 488–490 [30,40] 496.6 [30,41] 497 [25,27] 499 [42]	513	465.1	516.1	51.0	0.87	521

5	$[(C_2H_5)_3NH]Cl$	492			499–501 [43] 521–525 [24] 526–527 [30,44] 526–528 [29] 527–528 [45] 529 [29]	495	453.1	498.2	45.1	0.88	502
6	$[(C_2H_5)_4N]Cl$	544	398			536	516.4	548.2	31.8		
7	$[(n\text{-}C_3H_7)_2NH_2]Cl$	508			541–542 [46] 542–544 [47] 547.6–548 [48]	511	464.6	515.3	50.7	0.87	519
8	$[(n\text{-}C_3H_7)_3NH]Cl$	466	357	417	363 [39]	466	426.4	470.6	44.2	0.88	473
9	$[(n\text{-}C_3H_7)_4N]Cl$	482	340	386		482	463.9	488.3	24.4		
10	$[(CH_3)_2CHNH_3]Cl$	514	332 378	431	412–413 [49] 412.6 [30] 421–423 [50,51] 426 [27] 426–428 [30] 428–431 [52]	515	462.9	515.8	52.9	0.88	518
11	$\{[(CH_3)_2CH]_2NH_2\}Cl$	498		488	485–486 [53] 485–487 [54] 486–488 [30,55] 489.6–490 [56]	498	457.2	502.9	45.7	0.86	506
12	$[(n\text{-}C_4H_9)_2NH_2]Cl$	513			554 [25–27] 556 [40] 556–557 [47]	516	471.4	518.4	47.0	0.86	522
13	$[(n\text{-}C_4H_9)_3NH]Cl$	475				474	425.4	480.1	54.7	0.86	482
14	$[(n\text{-}C_4H_9)_4N]Cl$	473		351	314 [57]	473	451.2	479.6	28.4		
15	$[(CH_3)_2CHCH_2NH_3]Cl$	516	382	455	433 [30] 450 [58] 450–451 [59,60] 451–452 [61,62]	519	465.2	518.1	52.9	0.88	521
16	$[(CH_3)(C_2H_5)CHNH_3]Cl$	517	406	423	417–418 [50]	519	467.5	520.6	53.1	0.88	523

TABLE 2 (continued)

Substance ^{a}		Peak temperature ^{b} (K)						Temperature ^{b} (K)			Parameters of the onset of the second stage	
No.	Formula	DTG	DTA					$T_{0.1}$	$T_{0.82}$	ΔT_α		
			T_σ		T_m		T_p				α	T (K)
			This work	From literature	This work	From literature						
17	$[(CH_3)_3CNH_3]Cl$	514				543–553 [30] 546–548 [63] 563 [64] 563–564 [65] 583 [66,67]	517	466.5	519.8	55.3	0.88	524
18	$\{[(CH_3)_2CHCH_2]_2NH_2\}Cl$	497				533–538 [60] 535 [30]	500	456.5	507.1	50.6	0.87	512
19	$[(CH_3)_2CH(CH_2)_2NH_3]Cl$	520	345		494	482 [39] 488 [58,68] 489–490 [69] 491–492 [70] 493 [71]	522	471.4	525.6	54.2	0.88	528
20	$(c\text{-}C_6H_{11}NH_3)Cl$	522			478	475–476 [72] 476 [51] 476–477 [30] 476–478 [73] 477 [30] 477–478 [74–76] 478 [77] 478–480 [78] 478.6–479 [79]	524	473.6	525.7	52.1	0.86	527

						479 [30] 479–480.6 [30] 479.8 [80] 482–483 [81]						
21	$(C_4H_8NH_2)Cl$	541	337		431	390–392 [82]	543	485.5	543.2	57.7	0.86	545
22	$(C_5H_{10}NH_2)Cl$	525	510		515	503 [39] 510 [30] 515 [30,41] 516.6 [30] 517 [83] 517–518 [84] 517.6–519.1 [85] 518 [30,86] 519–520 [87] 520–521 [29] 521.5–523 [88]	529	476.1	528.9	52.8	0.86	531
23	$(C_7H_{13}NH)Cl$	555	349		525	547–548 [89] 589–591 [90] 642–647 [91]	557	505.7			0.82	563

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[a] The names of the compounds: 1 = *N*-methylmethanamine hydrochloride (or *N*-methylmethanaminium chloride); 2 = *N*,*N*-dimethylmethanamine hydrochloride; 3 = *N*,*N*,*N*-trimethylmethanaminium chloride; 4 = *N*-ethylethanamine hydrochloride; 5 = *N*,*N*-diethylethanamine hydrochloride; 6 = *N*,*N*,*N*-triethylethanaminium chloride; 7 = *N*-propyl-1-propanamine hydrochloride; 8 = *N*,*N*-dipropyl-1-propanamine hydrochloride; 9 = *N*,*N*,*N*-tripropyl-1-propanaminium chloride; 10 = 2-propanamine (isopropylamine) hydrochloride; 11 = *N*-(1-methylethyl)-2-propanamine (diisopropylamine) hydrochloride; 12 = *N*-butyl-1-butanamine hydrochloride; 13 = *N*,*N*-dibutyl-1-butanamine hydrochloride; 14 = *N*,*N*,*N*-tributyl-1-butanaminium chloride; 15 = 2-methyl-1-propanamine (isobutylamine) hydrochloride; 16 = 2-butanamine (*sec*-butylamine) hydrochloride; 17 = 2-methyl-2-propanamine (*tert*-butylamine) hydrochloride; 18 = 2-methyl-*N*-(2-methylpropyl)-1-propanamine (diisobutylamine) hydrochloride; 19 = 3-methyl-1-butanamine (isopentylamine) hydrochloride; 20 = cyclohexanamine hydrochloride; 21 = pyrrolidine hydrochloride; 22 = piperidine hydrochloride; 23 = 1-azabicyclo[2.2.2]octane (quinuclidine) hydrochloride. [b] The symbols were taken from ref. 20. T_p = temperature of the peak, T_σ = temperature of a solid-state phase transition, T_m = temperature of melting, T_α = temperature at which the degree of conversion is equal to α (i.e. $T_{0.1} = T_{\alpha=0.1}$), and $\Delta T_\alpha = T_{0.82} - T_{0.1}$.

RESULTS AND DISCUSSION

1. General characteristic of the thermal decomposition

Thermoanalytical curves recorded by a derivatograph for two compounds chosen as examples are shown in Fig. 1. The thermal analysis run for cyclohexanaminium chloride (Fig. 1A) is typical for all primary, secondary, and tertiary alkanaminium chlorides, whereas, the thermogram for *N,N,N*-tributyl-1-butanaminium chloride (Fig. 1B) is characteristic of all quaternary salts investigated.

To facilitate further discussion we compiled in Table 2 the essential parameters characterizing the thermal behaviour of all the compounds studied, derived from the thermal analysis curves, together with the available information from the literature. The characteristic feature of the thermal dissociation of all the compounds studied is that they undergo total volatilization upon heating to 700 K. Thermogravimetric curves reveal, however, that the decomposition of quaternary salts proceeds generally in one stage, whereas volatilization of the remaining compounds investigated is accomplished in two distinct steps. In the latter case, the first step, in which up to 90% of the sample volatilizes (Table 2), is followed by a slow one, seen as a "tail", in which the remaining part of the sample disappears. This effect has been observed also upon thermal dissociation of other compounds [10–12] and is explained by the mechanism of the process, which is discussed subsequently. The participation of side reactions (e.g. destruction of organic fragments of molecules [92]), which could also cause such an effect, has been excluded by performing previously-described tests [12]. It may, perhaps, be worthwhile to mention that noticeable decomposition of several amines (e.g. refs. 93–97) has been observed at temperatures much higher than those characteristic of the dissociation of appropriate chloride salts (Table 2).

Careful examination of thermograms reveals that additional endothermal peaks are seen on DTA curves of some of the compounds studied before the onset of decomposition. These effects can originate from polymorphic transitions or from melting. Some of these effects were identified on the basis of the literature data, i.e. peaks corresponding to solid-phase transitions, for the compounds No. 1, 2, 3, and peaks resulting from fusion, for the compounds No. 1, 10, 11, 15, 16, 19, 20, and 22. It may be also seen in Table 2 that for the above-listed compounds the derived temperatures for the transitions agree fairly well with those reported in the literature. There have been also reports regarding the fusion processes of several other alkanaminium chlorides, i.e. compounds No. 2, 3, 4, 5, 7, 12, 17, and 18, which were not, however, monitored in our experiments. The comparison of the literature m.p. values with the values of peak temperatures in DTG and DTA, as well as values of $T_{0.1}$ and $T_{0.82}$ reveals that these compounds decompose while melting. Moreover, for the majority of them the reported melting points correspond to temperatures at which the volatilization process is far advanced. It may be that weak thermal effects originating from fusion are masked by much stronger effects resulting from the volatilization process. The endothermic peaks occurring in DTA curves of the compounds No. 10, 15, 16, 19, and 22, below the m.p., were ascribed to the solid-phase transitions. For compounds No. 8, 9, 21, and 23 the temperatures of the endothermic effects were ascribed arbitrarily to the polymorphic transitions (lower values) and melting (higher values), since no convincing data regarding these transformations, if any at all, could be found in the literature. An attempt at determining m.p. values for the last compounds by a standard capillary method failed owing to their highly hygroscopic nature. The thermal effect for *N,N,N*-triethylethanaminium chloride seen at 398 K was ascribed to the polymorphic transformation since Thompson and Kraus [98] noted that the compound decomposed without melting. On the other hand, the effect for *N,N,N*-tributyl-1-butanaminium chloride occurring at 351 K was ascribed to melting on the basis of the work of Coker et al. [57], although the authors reported a much lower value for the m.p. than that found in the present work. The effect seen in the TG curve of the latter compound (Fig. 1B), at the beginning of analysis, results from the absorption of water from the environment and it was sometimes observed in thermal analyses of highly hygroscopic derivatives. The compounds studied presumably undergo phase transitions below room temperature also. Unfortunately, these transformations could not be detected with the method applied.

The temperatures of thermolysis, namely, T_p (from DTG and DTA), $T_{0.1}$, $T_{0.82}$, and ΔT_α are the feature characteristic for a given compound; nevertheless, some general regularities can be revealed. For branched primary alkanaminium chlorides values of all the above-mentioned parameters are almost the same. They are also comparable with those found in the case of appropriate unbranched alkanamine hydrochlorides [10]. This implies that the structure of an alkyl group has only a minor effect on the thermal behaviour of primary alkanaminium chlorides. The characteristic temperatures of thermolysis generally decrease on moving from secondary to tertiary derivatives. On the other hand, T_p, $T_{0.1}$, $T_{0.82}$, and ΔT_α show rather complex dependencies on the length of the alkyl group. For the quaternary salts the values of all the above-mentioned parameters decrease significantly with an increase of the length of an alkyl substituent. Moreover, the characteristic temperatures of the thermal decomposition of these derivatives are much higher in comparison with those for other compounds studied. Also peak temperatures in DTG are higher than those in DTA. In the case of primary [10], secondary, and tertiary alkanamine hydrochlorides the last dependence is reversed.

Not too much attention has been devoted in the past to the thermoanalytical investigations of alkanaminium chlorides. In the work of Myao

Tsin-Shen and Tronev [99] the DTA investigations of $C_2H_5NH_2 \cdot HCl$, $(C_2H_5)_2NH \cdot HCl$, and $(C_2H_5)_3N \cdot HCl$ have been reported. Unfortunately, our results differ markedly from those of the above-mentioned authors. We believe that these discrepancies result mainly from the differences in the experimental conditions.

2. *Nature of the thermal processes*

Numerous investigations proved that alkanaminium chlorides behave in condensed phases as typical ionic substances [8,27,100]. It can thus be expected that the thermal decomposition process followed by the transfer of molecules from the condensed to gaseous phase must involve several stages. The mechanism of volatilization of primary alkanaminium chlorides has been thoroughly discussed in our previous work [10]. It may be assumed that the same mechanism also holds in the case of secondary and tertiary alkanamine hydrochlorides. Therefore, the overall process can be summarized with the equation

$$(R_pNH_{4-p})Cl_{(l,c)} \rightarrow R_pNH_{3-p(g)} + HCl_{(g)} \qquad (1)$$

where R denotes alkyl group and $p = 0$–3.

There are only few reports regarding thermal decomposition of quaternary alkanaminium chlorides [2,30,101] and none of them is primarily concerned with the mechanism of the process. Following those reports we assumed that the overall process proceeds according to the equation

$$(R_4N)Cl_{(l,c)} \rightarrow R_3N_{(g)} + RCl_{(g)} \qquad (2)$$

A similar pathway to that shown by eqn. (2) has been also predicted for the thermal decomposition of primary, secondary and tertiary alkanamine hydrochlorides [2]

$$(R_pNH_{4-p})Cl_{(l,c)} \rightarrow R_{p-1}NH_{4-p(g)} + RCl_{(g)} \qquad (3)$$

where $p = 1$–3. We will discuss this issue in a subsequent section on the basis of the thermochemistry and kinetics of appropriate processes.

Rough estimations made on the basis of the Clausius–Clapeyron equation using appropriate values of boiling points [102] and heats of vaporization [103] for amines prove that all the products formed in reactions (1–3) appear in the gaseous phase. However, this information does not give an answer to the question of whether the products behave as kinetically free fragments or whether they interact with other forming aggregates. The formation of weak complexes between amines and HCl can be expected on the basis of theoretical considerations [4–6], as well as certain experimental evidence [7,9]. Furthermore, some amines may interact with each other in the gaseous phase forming dimers [104]. It is worth mentioning that some theoretical considerations tend also to confirm this hypothesis [14,105].

3. Thermodynamics of the thermal decomposition

In the previous work concerned with the thermochemistry of mono-1-alkanaminium chlorides we demonstrated that dynamic thermogravimetric data can be successfully used for the evaluation of the enthalpy of their thermal dissociation [10]. For this purpose the following equation was used

$$\ln \alpha = -\frac{\Delta H_v}{2RT} + \text{const} \tag{4}$$

where ΔH_v is the enthalpy of the thermal process and R denotes the gas constant. The main premise of this method is that the system attains equilibrium at a given temperature, T. This implies that the only energy barrier existing for the process is the thermodynamical one, i.e. ΔH_v. Then the experimental degree of conversion, α, is equal to P/P_0, where P is the equilibrium vapor pressure at a given T value and P_0 is the atmospheric pressure. Equation (4) results directly from the application of the Van't Hoff rule to reactions (1), (2), or (3).

To meet the above requirements the thermal analyses were carried out in such a way as to eliminate all side factors which could affect the equilibrium conditions. Thus, the analyses were performed at moderate heating rate and using as small a sample weight as possible. Furthermore, the samples were always placed in thin layers on a relatively large surface to avoid side reactions and to enable free diffusion of gaseous products.

The derived values of ΔH_v are summarized in Table 3. For a few compounds studied the evaluated enthalpies of the thermal dissociation can be compared directly with those reported in the literature. The agreement is rather poor, partly because some of the literature data does not seem to be very adequate. Much more reliable sources of information are ΔH_v values for reactions (1) and (2) derived from the standard enthalpies of formation of reactants. The latter values are always higher than those derived in this work in the case of primary, secondary, and tertiary alkanamine hydrochlorides and these discrepancies will be discussed subsequently. None the less, ΔH_v values obtained by both ways mentioned above show similar trends. For quaternary salts both calculated values of ΔH_v from values of the standard enthalpies of formation, as well as those evaluated from the data of Smith and Calvert [101] are surprisingly low in comparison with the values of the enthalpy for reaction (2) from this work. These differences are too high to be accounted for by non-perfect experimental conditions. The only explanation of these discrepancies is that reaction (2) requires fairly high activation barriers to be overcome over that resulting from the thermodynamical requirements. This implies that the process proceeds far from the equilibrium conditions and is fully supported by the data in Table 2.

The values listed in the last column of Table 3 represent the enthalpy changes for the release of gaseous chloroalkanes and amines from alkanaminium chlorides. For primary [10], secondary, and tertiary derivatives these values are comparable to the ΔH_v values calculated for reaction (1). It could indicate that both reaction (1) and (3) might proceed simultaneously and this, of course, would cause the complex course of the thermal decomposition of these derivatives. The thermoanalytical investigations apparently demonstrate, however, that the process does not exhibit the complex nature.

TABLE 3

Thermochemistry of the thermal dissociation of alkanaminium chlorides

Substance No. (Table 2)	Const [a]	ΔH_v [a] (kJ mol^{-1})	Enthalpy of volatilization (kJ mol^{-1})		
			From literature [b]	Calculated from the standard enthalpies of formation at 298 K [c]	
				From eqn. (1)	From eqns. (2) or (3)
1	16.9	149	95.4 (439–533) [25] 144.0 (533–569) [25]	180.3	186.1
2	17.6	145		165.5 * 167.3 **	176.5 * 182.8 **
3	36.0	364	167 (463–506) [101]		168.8 * 170.3 **
4	19.2	167	177.4 (498–560) [25]	190.5 * 193.3 ** 193.8 *** 194.7 ****	195.8 * 198.6 ** 199.1 *** 200.0 ****
5	21.3	178		194.6 * 197.5 ** 202.4 ***	195 * 197.9 ** 202.8 ***
6	33.7	308			195.9 * 209.1 **
7	19.6	169		181.2	186.9
8	20.2	159		193.1	198
9	40.3	327			206.6
10	18.4	159			
11	21.0	177			
12	21.0	182	116.8 (554–566) [25]		
13	16.7	134			
14	33.3	265			
15	18.5	160			
16	18.6	162			
17	18.6	162			
18	20.5	173			
19	18.4	162			
20	19.2	169		210.9	198.5
21	17.6	160			
22	19.4	171			
23	19.1	179			

(Table 3 footnotes)

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[a] Values of ΔH_v and const were calculated from eqns. (1) or (2) within a range of α from 0.1 to 0.82 (0.74). The linear correlation coefficient (r) was always better than 0.995 in the case of primary, secondary, and tertiary salts. For quaternary alkanaminium chlorides the values of r were always somewhat lower. [b] The temperature range, in K, is given in parentheses. [c] Values used in the calculations (kJ mol^{-1}): $\Delta H^0_\mathrm{f,g}[\mathrm{HCl}] = -92.3$ [102,106]; $\Delta H^0_\mathrm{f,g}[\mathrm{CH_3Cl}] = -82.0$ [107]; $\Delta H^0_\mathrm{f,g}[\mathrm{C_2H_5Cl}] = -112.1$ [107]; $\Delta H^0_\mathrm{f,g}[n\text{-}\mathrm{C_3H_7Cl}] = -132.4$ [107]; $\Delta H^0_\mathrm{f,g}[\text{c-}\mathrm{C_6H_{11}Cl}] = -163.6$ [107]; $\Delta H^0_\mathrm{f,g}[\mathrm{NH_3}] = -46.1$ [102,106]; $\Delta H^0_\mathrm{f,g}[\mathrm{CH_3NH_2}] = -23.0$ [14,106,107]; $\Delta H^0_\mathrm{f,g}[\mathrm{(CH_3)_2NH}] = -18.5$ [107]; $\Delta H^0_\mathrm{f,g}[\mathrm{(CH_3)_3N}] = -23.7$ [107]; $\Delta H^0_\mathrm{f,g}[\mathrm{C_2H_5NH_2}] = -47.5$ [107]; $\Delta H^0_\mathrm{f,g}[\mathrm{(C_2H_5)_2NH}] = -72.6$ [107]; $\Delta H^0_\mathrm{f,g}[\mathrm{(C_2H_5)_3N}] = -92.8$ [107]; $\Delta H^0_\mathrm{f,g}[n\text{-}\mathrm{C_3H_7NH_2}] = -70.2$ [107]; $\Delta H^0_\mathrm{f,g}[(n\text{-}\mathrm{C_3H_7})_2\mathrm{NH}] = -116$ [14,107]; $\Delta H^0_\mathrm{f,g}[(n\text{-}\mathrm{C_3H_7})_3\mathrm{N}] = -161.0$ [14,107]; $\Delta H^0_\mathrm{f,g}[\text{c-}\mathrm{C_6H_{11}NH_2}] = -105$ [14]; $\Delta H^0_\mathrm{f,c}[\mathrm{(CH_3)_2NH \cdot HCl}] = -291.1$ [108]; $\Delta H^0_\mathrm{f,c}[\mathrm{(CH_3)_3N \cdot HCl}] = -281.5$ * [109] and -283.3 ** [108]; $\Delta H^0_\mathrm{f,c}[\mathrm{(CH_3)_4NCl}] = -274.5$ * [110] and -276.0 ** [108]; $\Delta H^0_\mathrm{f,c}[\mathrm{(C_2H_5)_2NH \cdot HCl}] = -355.4$ * [111], -358.2 ** [112], -358.7 *** [107], and -359.6 **** [113]; $\Delta H^0_\mathrm{f,c}[\mathrm{(C_2H_5)_3N \cdot HCl}] = -379.7$ * [107], -382.6 ** [114], and -387.5 *** [111]; $\Delta H^0_\mathrm{f,c}[\mathrm{(C_2H_5)_4NCl}] = -400.8$ * [115] and -414 ** [111]; $\Delta H^0_\mathrm{f,c}[(n\text{-}\mathrm{C_3H_7})_2\mathrm{NH \cdot HCl}] = -389.5$ [116]; $\Delta H^0_\mathrm{f,c}[(n\text{-}\mathrm{C_3H_7})_3\mathrm{N \cdot HCl}] = -446.4$ [116]; $\Delta H^0_\mathrm{f,c}[(n\text{-}\mathrm{C_3H_7})_4\mathrm{NCl}] = -500$ [116]; $\Delta H^0_\mathrm{f,c}[\text{c-}\mathrm{C_6H_{11}NH_2 \cdot HCl}] = -408.2$ [117].

Moreover, one might expect the existence of a fairly high activation barrier for reaction (3) on the basis of the previous considerations for quaternary salts. Since the applied method of investigation enables the excitation of only vibrational degrees of freedom in the molecule, the most probable primary dissociation pathway is that which requires the lowest value of energy. These facts, as well as numerous similarities in the thermal behaviour of primary, secondary, and tertiary amine hydrochlorides and that of $\mathrm{NH_4Cl}$ tend to confirm that the thermal decomposition of all these compounds follows eqn. (1).

4. *Kinetics of the thermal dissociation*

For the description of the kinetics of volatilization of primary, secondary, and tertiary alkanamine hydrochlorides we invoked the phenomenological theory outlined by Jacobs and Russell-Jones [118]. The main premise of this method is that the migration of molecules over the surface of a condensed phase followed by their diffusion through the gas phase determine the kinetics of the whole process. Despite some criticism of this approach [119] it has been proved that this model satisfactorily describes the kinetics of non-isothermal dissociation of ammonium and several mono-1-alkanamine hydrochlorides [10], hexachlorostannates [11], and hydrochlorides of aromatic bases [12]. The detailed discussion of this method and its adaptation to the non-isothermal conditions have been presented elsewhere [10,118]. The final form of the integral equation, adequate for linearly increasing temperature conditions, is given below.

$$\left(X_2T-\left(\frac{\Delta}{a_0}\right)\right)\left[1-(1-\alpha)^{1/3}\right]+\tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]$$
$$-\left(\frac{\Delta}{a_0}\right)^2\ln\left[\frac{(1-\alpha)^{1/3}+(\Delta/a_0)}{1+(\Delta/a_0)}\right]=\frac{1}{3}\left(\frac{X_1}{\Phi}\right)T^{3/2}\,e^{-E/2RT} \qquad (5)$$

where X_1, X_2, and E are the constants and E identifies the apparent activation energy for the process, Φ is the heating rate, a_0 represents the initial radius of particles from which the volatilization process occurs, and Δ denotes the distance between collisions (i.e. a distance which a molecule travels after leaving the condensed phase, before a collision occurs). At moderate pressures of a foreign gas, $P \approx$ atmospheric pressure, $\Delta \ll a_0$, and the influence of this parameter on the kinetics of the process is negligible. Then, eqn. (5) can be simplified to the form

$$X_2T\left[1-(1-\alpha)^{1/3}\right]+\tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]=\tfrac{1}{3}(X_1/\Phi)T^{3/2}\,e^{-E/2RT} \qquad (6)$$

which actually describes the kinetics of the first, fast step of the thermal dissociation of primary, secondary, and tertiary alkanamine hydrochlorides.

TABLE 4

Kinetic constants for the volatilization of alkanamine hydrochlorides

Substance No. (Table 2)	From the Jacobs and Russell-Jones model: eqn. (6)			From the surface contracting area equation: $1-(1-\alpha)^{1/2}=Z(T/\Phi)\,e^{-E^*/RT}$	
	E (kJ mol^{-1})	X_1 (K$^{-1/2}$ s^{-1})	X_2 (K^{-1})	E^* (kJ mol^{-1})	Z (s^{-1})
1	138	30.7	-5.6×10^{-4}	80.8	8.9×10^{3}
2	118	7.04	-7.9×10^{-4}	79.1	2.3×10^{4}
4	164	1050	-3.6×10^{-4}	91.0	1.4×10^{5}
5	168	3340	-4.4×10^{-4}	97.8	1.5×10^{6}
7	148	140	-6.0×10^{-4}	92.4	2.1×10^{5}
8	148	1030	-3.3×10^{-4}	87.4	4.8×10^{5}
10	152	259	-3.8×10^{-4}	86.9	5.4×10^{4}
11	178	11000	-1.6×10^{-4}	97.1	1.0×10^{6}
12	182	9070	-1.6×10^{-4}	100.0	1.0×10^{6}
13	127	42.6	-5.3×10^{-4}	72.7	7.5×10^{3}
15	161	783	-1.6×10^{-4}	87.4	5.4×10^{4}
16	149	141	-4.8×10^{-4}	88.6	6.6×10^{4}
17	144	73.3	-6.1×10^{-4}	88.3	6.6×10^{4}
18	169	3630	-2.1×10^{-4}	93.2	4.1×10^{5}
19	159	506	-0.91×10^{-4}	88.4	5.2×10^{4}
20	161	492	-4.3×10^{-4}	92.5	1.3×10^{5}
21	151	76.2	-5.3×10^{-4}	87.2	2.0×10^{4}
22	158	273	-5.8×10^{-4}	93.6	1.5×10^{5}
23	151	37.5	-6.9×10^{-4}	96.3	8.0×10^{4}

Numerical values of the kinetic constants, giving the best fit of eqn. (6) to the experimental α vs. T dependencies, were found using previously described procedure [10,11]. These values are listed in Table 4.

From the formal point of view the volatilization of primary, secondary, and tertiary alkanamine hydrochlorides can be considered as a chemical reaction. Thus, the kinetics of the process should follow the integral equation [120]

$$g(1-\alpha)=Z\left(\frac{T}{\Phi}\right)\mathrm{e}^{-E^*/RT} \tag{7}$$

where $g(1-\alpha)$ denotes the mathematical function describing the kinetic model for the process (see ref. 19, Table 1), E^* expresses the apparent activation energy, and Z is the constant. The application of the standard least squares procedure to the experimental α vs. T data points permitted the calculation of E^* and Z for various $g(1-\alpha)$ functions [19,121]. These calculations revealed that usually several reaction models fit very well with the experimental thermogravimetric curves. In Table 4 only the kinetic constants for the surface contracting area mechanism (R2) are given, since it has been found that this model describes satisfactorily the kinetics of sublimation of some ammonium salts under atmospheric pressure [118,122]. Also our studies proved that experimental data correlate fairly well with the R2 reaction model.

The values of E from the Jacobs and Russell-Jones equation are very close to the appropriate values of the enthalpy of volatilization. This fact could indicate that the process does not require overcoming any activation barrier over that resulting from the thermochemical requirements. It would also mean that volatilization of alkanamine hydrochlorides takes place near the equilibrium conditions. The meaning of X_1 and X_2 is not defined precisely, but both constants should be positive. The data in Table 4 show, however, that this is actually observed only for X_1. All the values of X_2 are negative. This discrepancy may result from the neglect of two terms holding Δ/a_0 in eqn. (6), which are formally negative (see eqn. (5)). These facts imply that both X_1 and X_2 in eqn. (6) should be considered rather as mathematical constants without true physical significance.

Perhaps the most important feature of the Jacobs and Russell-Jones equation is that it predicts the decrease of the rate of the volatilization with the decrease of the geometric surface area of a condensed phase. This effect had originally been predicted by Fuchs [123] and its existence has been proved later by other authors [118,124,125]. However, except in our studies [10–12], this phenomenon has not been so far reported in non-isothermal investigations.

As was mentioned earlier, if Δ/a_0 is small as is valid for the first step of volatilization, an adequate form for the description of the kinetics of the process is eqn. (6). However, at the end of the process the mean free path for

TABLE 5

The ratio of $E^*/\Delta H_v$ for various reaction models

Mechanism of the process [a]	R1	R2	R3	P1	P2	P3	P4	F1	A2	A3	D1	D2	D3	D4
$E^*/\Delta H_v$	0.48	0.55	0.57	0.35	0.31	0.23	0.10	0.63	0.30	0.19	0.98	0.83	1.17	1.10

[a] For details see ref. 19, Table 1.

the molecules increases in comparison with the dimensions of drops or crystals, and Δ approaches a_0 in magnitude. This causes a gradual decrease of the rate of the process as both terms holding Δ/a_0 in eqn. (5) are negative. The above effect is clearly seen in thermogravimetric curves of all alkanamine hydrochlorides studied. We also proved that this phenomenon is of a general nature and occurs upon non-isothermal volatilization of a number of other compounds [10–12].

The question remains of how to interpret the values of kinetic constants for alkanamine hydrochlorides derived on the basis of eqn. (7). Our experience suggests that Z should be treated only as a purely mathematical constant. On the other hand, since the exponential term in eqn. (7) links directly to the Arrhenius equation the values of E^* can be considered as an apparent activation energy for the process. Reviewing the kinetic calculations it is noticed that values of E^* show the same trends as appropriate ΔH_v values. Furthermore, we found that the ratios of $E^*/\Delta H_v$ are almost identical at a given kinetic model for all primary, secondary, and tertiary alkanamine hydrochlorides (Table 5). It is, however, surprising that values of E^* are usually much lower than appropriate values of the enthalpy change for the process. Only E^* values for diffusion mechanisms are comparable to those of ΔH_v. For the two reaction models often proposed for the description of the kinetics of dissociative sublimation, namely R1 [126–128] and R2 [118,122], the values of E^* are only equal to 0.48 and 0.55 of the ΔH_v values, respectively. Many efforts have been made in the past to explain these low values of E^* [127–129]. However, it seems unlikely that the molecule can reach a high energy level resulting from ΔH_v if the rate determining step has such a low activation barrier. One could, thus, expect a much more complex nature for the process. On the other hand, the apparent difficulties in the interpretation of E^* can be concealed in eqn. (7). Perhaps it would be more adequate to consider this equation against two molecules of gaseous products. Such a concept would require that the transition state for the volatilization of alkanamine hydrochlorides is a loosely bonded complex of amine and HCl. Then, following the suggestion of Meschi and Searcy [130], the exponent in the kinetic equation should admit the form: $\exp(-E^*/2RT)$ and all the values of E^* would be a factor of 2 higher compared with those derived from eqn. (7). The above considerations clearly demonstrate that eqn. (7) presents a rather purely formal approach to this

TABLE 6

Kinetics of the thermal dissociation of quaternary alkanaminium chlorides [a]

Kinetic model for the process [b]	Kinetic constants							
	$[(CH_3)_4N]Cl$		$[(C_2H_5)_4N]Cl$		$[(n\text{-}C_3H_7)_4N]Cl$		$[(n\text{-}C_4H_9)_4N]Cl$	
	E^*	Z	E^*	Z	E^*	Z	E^*	Z
R1	177	2.8×10^{11}	149	2.6×10^{10}	160	2.0×10^{13}	129	1.5×10^{10}
R2	204	3.8×10^{13}	173	2.9×10^{12}	184	5.7×10^{15}	149	1.5×10^{12}
R3	214	2.0×10^{14}	181	1.4×10^{13}	193	4.0×10^{16}	156	6.8×10^{12}
F1	235	4.9×10^{16}	200	3.0×10^{15}	213	1.9×10^{19}	172	1.3×10^{15}
D1	359	1.3×10^{27}	303	1.2×10^{25}	323	6.2×10^{30}	262	4.2×10^{24}
D3	432	6.2×10^{32}	367	3.3×10^{30}	391	2.6×10^{37}	316	8.4×10^{29}
D4	406	2.3×10^{30}	344	1.5×10^{28}	366	4.4×10^{34}	296	4.3×10^{27}

[a] Kinetic constants were calculated from eqn. (7). E^* = apparent activation energy (kJ mol^{-1}); Z = constant (s^{-1}). [b] For details see ref. 19, Table 1.

problem. Much more realistic seems to be the Jacobs and Russell-Jones model which predicts the activation energy values in accord with well known physical significance of this magnitude.

To examine the kinetics of the thermal decomposition of quaternary salts we used a standard procedure based on eqn. (7). The kinetic constants for some selected mechanisms of the process are listed in Table 6. It is interesting that we obtained the highest values of the correlation coefficient always in the case of the F1 mechanism. Also R2, R3, A2, A3, D1, D3, and D4 reaction models correlate fairly well with the experimental thermogravimetric curves. Unfortunately, the adopted approach to the problem was purely formal and the derived values of an apparent activation energy do not seem to provide reliable information on the height of the energetic barrier for the thermal decomposition process.

5. Thermochemical characteristics

Many thermochemical quantities for the compounds studied can be derived from a simple Hess's law. The various relations between these quantities are usually presented in the form of a thermochemical cycle. In our latest work devoted to the thermal properties of primary 1-alkanamine hydrochlorides we presented such a cycle [10]. The thermochemical relationships derived in that work are also valid for all primary, secondary, and tertiary alkanamine hydrochlorides and we therefore used them for the evaluation of the following quantities

$$\Delta H^0_{f,c}\left[(R_pNH_{4-p})Cl\right] = \Delta H^0_{f,g}\left[R_pNH_{3-p}\right] + \Delta H^0_{f,g}[HCl] - \Delta H^0_v \qquad (8)$$

$$\Delta H^0_{f,g}\left[R_pNH^+_{4-p}\right] = \Delta H^0_{f,g}\left[R_pNH_{3-p}\right] + \Delta H^0_{f,g}[H^+] - PA\left[R_pNH_{3-p}\right] \qquad (9)$$

$$U^0\left[(R_pNH_{4-p})Cl\right] = \Delta H^0_{f,g}\left[R_pNH^+_{4-p}\right] + \Delta H^0_{f,g}[Cl^-] - \Delta H^0_{f,c}\left[(R_pNH_{4-p})Cl\right] - 2RT \qquad (10)$$

All magnitudes in eqns. (8)–(10) refer to 298 K and 1 atm: ΔH_f denotes the enthalpy of formation of a given species ($p = 1$–3); $U + 2RT$ is the lattice enthalpy; U represents the lattice energy; PA is the proton affinity of an amine; and ΔH_v identifies the enthalpy of volatilization.

The ΔH_v values derived in this work do not refer to 298 K and therefore were modified according to the equation

$$\Delta H^0_{v,298} = \Delta H_v + \Delta H^0_{fn} + \Sigma \Delta H^0_\sigma - \int_{298}^{T} \Delta C^0_p \, dT \qquad (11)$$

where ΔH_v is the enthalpy of volatilization from eqn. (4); ΔH^0_{fn} expresses the enthalpy of fusion; the term $\Sigma \Delta H^0_\sigma$ arises from any polymorphic transitions which these compounds may undergo between 298 K and the onset of the fusion or volatilization process; and the term $\int_{298}^{T} \Delta C^0_p \, dT$ accounts for the change of enthalpy resulting from the changes of heat capacities of reactants. Since the pertinent data for ΔH^0_{fn} are not available we estimated the numerical values of this magnitude using empirical relationship relating to the entropy of fusion: $\Delta S^0_{fn} = \Delta H^0_{fn}/T_m = \text{const}$. The value of ΔS^0_{fn} was assumed to be 13.6 J mol^{-1} K^{-1} [10] on the basis of the available literature data for mono-1-alkanaminium chlorides [131,132]. Taking this value and temperatures of melting from Table 2 we evaluated the enthalpies of fusion. They are listed in Table 7. For compounds No. 2, 4, 5, 7, 12, 13, 17, and 18 the term ΔH^0_{fn} was ignored since they melt and decompose simultaneously and the process of fusion presumably does not affect thermodynamics of decomposition of these derivatives. None of the heats of phase transitions for alkanamine hydrochlorides studied are available. Such transitions amount usually to values ca. 4 kJ mol^{-1} [10,131,133], and this value has been arbitrarily chosen for this quantity (Table 7). The magnitude and sign of the heat capacity term is also difficult to assess in the absence of appropriate C^0_p data for the majority of salts and gaseous products. On the basis of $C^0_p = f(T)$ dependencies for NH_4Cl [134], $(CH_3NH_3)Cl$ [133], ammonia [134], methanamine [134], and HCl [134] we found that ΔC^0_p for the volatilization of both ammonium chloride and methanaminium chloride vary with temperature similarly and can be approximated with the equation: $7.2 - 0.133T$ (in J mol^{-1} K^{-1}). We assumed that this relationship also holds for the remaining alkanamine hydrochlorides. Some idea of the validity of this assumption may be gauged from the fact that the expected increase of the heat capacity caused by an increase in the size of an alkyl group should be similar for both salts and appropriate amines. It may, perhaps, be worthwhile to mention that the above regularity regarding ΔC^0_p does not exist upon dissociation of alkanamine hydrochlorides in aqueous solutions [135,136]. In the latter case, however, the reported differences are mostly due to the interactions of amines and their cations with the solvent. The estimated values of the heat capacity term are shown in Table 7, and the modified values of ΔH^0_v are listed in Table 8.

TABLE 7

Ancillary data for the evaluation of thermochemical parameters [a]

Substance No. (Table 2)	$(R_pNH_{4-p})Cl$			R_pNH_{3-p}		$R_pNH_{4-p}^+$
	ΔH_{fn}^0	$\Sigma\Delta H_\sigma^0$	$\int_{298}^{T_{0.1}} \Delta C_p^0 \, dT$	$\Delta H_{f,g}^0$ [b]	PA [c]	$\Delta H_{f,g}^0$
1	6.1	4	−7.4	−18.5	934	584
2		4	−5.9	−23.7	950	563
4			−7.3	−72.6	953	511
5			−6.6	−92.8	978	465
7			−7.2	−116	961	459
8	5.7	4	−5.3	−161	988	387
10	5.9	8	−7.2	−83.8	929	523
11	6.6		−6.8	−144	969	423
12			−7.6	−156.6	966	414
13			−5.2	−222	993	321
15	6.2	4	−7.3	−98.8	930	507
16	5.7	4	−7.4	−104.8	934	497
17			−7.4	−120.9	938	477
18			−6.8	−179.2	968	389
19	6.7	4	−7.6	−121	932	483
20	6.5		−7.7	−105	937	494
21	5.9	4	−8.4	−3.4	950	583
22	7.0	4	−7.9	−48.9	954	533
23	7.1	4	−9.6	−4.2	979	553

[a] All values in kJ mol^{-1}. [b] The standard enthalpies of formation of gaseous amines at 298 K were taken from refs. 14 and 107. The value of $\Delta H_{f,g}^0$ for 3-methyl-1-butanamine was estimated by the Benson's group additivity method [137]. [c] Proton affinities were taken from ref. 138 and corrected relative to the PA value for ammonia of 860 kJ mol^{-1} [139]. The value of PA for 3-methyl-1-butanamine was assumed to be 932 kJ mol^{-1} [14,139].

To evaluate thermochemical quantities from eqns. (8)–(10) we used $\Delta H_{f,g}^0[R_pNH_{3-p}]$ and $PA[R_pNH_{3-p}]$ values listed in Table 7. Further, we assumed for $\Delta H_{f,g}^0[HCl]$, $\Delta H_{f,g}^0[H^+]$, and $\Delta H_{f,g}^0[Cl^-]$ values equal to (in kJ mol^{-1}): −92.3 [102,106,134], 1536.2 [102,106,134], and −233.1 [106], respectively. The derived standard enthalpies of formation and crystal lattice energies for alkanamine hydrochlorides studied are presented in Table 8.

The values of the enthalpy of volatilization of amine hydrochlorides examined in this work generally show similar regularities to those observed for mono-1-alkanaminium chlorides. The ΔH_v values for branched primary alkanamine hydrochlorides are comparable with those for unbranched derivatives [10]. Moreover, they are almost the same for both groups of compounds and the observed differences are within experimental uncertainties. A gradual increases of ΔH_v values with an increase of the size of an alkanaminium cation can be observed. This regularity is particularly pronounced in the case of cyclic derivatives, but does not hold, however, for

TABLE 8

Thermochemical quantities for alkanaminium chlorides at 298 K [a]

Substance [b]		ΔH_v^0 (kJ mol^{-1})	$\Delta H^0_{f,c}$ (kJ mol^{-1})		U^0 (kJ mol^{-1})		r_K (nm)
No.	Formula		This work	From literature	This work	From literature	
1	$(Me_2NH_2)Cl$	167	−278	−291.1 [108]	624	627 [108]	0.188
2	$(Me_3NH)Cl$	155	−271	−281.5 [109] −283.3 [108]	596	596 [108]	0.208
3	$(Me_4N)Cl$	(166)	(−272)	−274.5 [110] −276.0 [108]	(576)	502 [115] 523 [140] 548 [141] 552.8 [142] 566 [108]	(0.223)
4	$(Et_2NH_2)Cl$	174	−339	−355.4 [111] −358.2 [112] −358.7 [107] −359.6 [113]	612	617 [111]	0.197
5	$(Et_3NH)Cl$	185	−370	−379.7 [107] −382.6 [114] −387.5 [111]	597	607 [111]	0.207
6	$(Et_4N)Cl$	(196)	(−401)	−400.8 [115] −414 [111]	(575)	422 [115] 641 [111]	(0.224)
7	$(n\text{-}Pr_2NH_2)Cl$	176	−384	−389.5 [116]	605	593 [116]	0.202
8	$(n\text{-}Pr_3NH)Cl$	174	−427	−446.4 [116]	576	575 [116]	0.223
9	$(n\text{-}Pr_4N)Cl$	(182)	(−475)	−500 [116]	(546)	550 [116]	(0.248)
10	$(i\text{-}PrNH_3)Cl$	180	−356		641		0.177
11	$(i\text{-}Pr_2NH_2)Cl$	190	−426		611		0.197
12	$(n\text{-}Bu_2NH_2)Cl$	190	−439		615		0.195
13	$(n\text{-}Bu_3NH)Cl$	139	−453		536		0.257
14	$(n\text{-}Bu_4N)Cl$	(158)	(−534)		(521)		(0.271)
15	$(i\text{-}BuNH_3)Cl$	178	−369		638		0.179
16	$(s\text{-}BuNH_3)Cl$	179	−376		635		0.181
17	$(t\text{-}BuNH_3)Cl$	169	−382		621		0.190
18	$(i\text{-}Bu_2NH_2)Cl$	180	−452		603		0.203
19	$(i\text{-}PentNH_3)Cl$	180	−393		638		0.179
20	$(c\text{-}HexNH_3)Cl$	183	−380	−408.2 [117]	636		0.181
21	Pyr·HCl	178	−274		619		0.192
22	Pip·HCl	190	−331		626		0.187
23	Quin·HCl	200	−297		612		0.197

[a] Values obtained by extrapolation or estimated are given in parentheses. [b] For names of the compounds see Table 2.

$(Me_pNH_{4-p})Cl$. Also the enthalpy of volatilization of *N*,*N*-dibutyl-1-butanaminium chloride is surprisingly low.

The enthalpies of formation of crystalline alkanaminium chlorides present a feature characteristic for a given compound and preliminary examination of the data in Table 8 does not show any regularity. A closer inspection

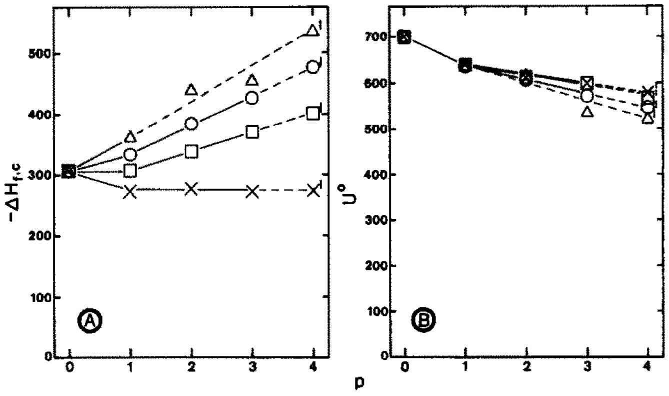

Fig. 2. The enthalpies of formation (A) and crystal lattice energies (B), both in kJ mol^{-1}, for $[(C_nH_{2n+1})_pNH_{4-p}]Cl$ against the number of alkyl groups (p): ×, $n = 1$; □, $n = 2$; ○, $n = 3$; △, $n = 4$; values with comma were obtained by extrapolation or estimated.

reveals, however, that the $\Delta H_{f,c}^{0}$ values for unbranched alkanaminium chlorides, of general formula $(R_pNH_{4-p})Cl$, show interesting trends against the number of R groups. Thus, we plotted in Fig. 2 values of $\Delta H_{f,c}^{0}$ derived from this work together with appropriate data taken from ref. 10 (the enthalpies of formation of mono-1-alkanaminium chlorides from our previous work were modified using more reliable data for the enthalpies of formation of amines [14,107]). With the exception of ammonium chloride these values decrease proportionally with the number of R substituents in the amine molecule, i.e. if R = Me, Et, and *n*-Pr. Similar regularities have been also observed by other authors [108,111,116]. Following the suggestion of these authors we assumed that analogous trends are valid for appropriate quaternary salts. Thus, extrapolating $\Delta H_{f,c}^{0}$ values the standard enthalpies of formation of $(Me_4N)Cl$, $(Et_4N)Cl$, and $(n\text{-}Pr_4N)Cl$ (Table 8) are obtained. Unfortunately, this regularity does not hold for *n*-Bu substituted derivatives and the value of $\Delta H_{f,c}^{0}[(n\text{-}Bu_4N)Cl$ cannot be estimated by the above procedure.

To facilitate discussion of the crystal lattice energy problem, we invoked an approximate method developed originally by Kapustinskii [143] and improved later by Yatsimirskii [144]. Following these authors the crystal lattice energy can be expressed with the equation [144]

$$U = 120.2\frac{((\Sigma n)Z_K Z_A)}{(r_K + r_A)}\left[1 - \left(\frac{0.0345}{r_K + r_A}\right) + 0.087(r_K + r_A)\right] \quad \text{in kJ mol}^{-1} \tag{12}$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule; Z_K and Z_A denote the numerical values of the charges of cation and anion, respectively; and r_K and r_A are the "thermochemical" ionic radii (in nm). Assuming an r_{Cl^-} value equal to 0.172 nm [145] we derived the values of r_K listed in Table 8.

The crystal lattice energies generally decrease with an increase of both the size of an alkyl substituent and the number of alkyl groups at the nitrogen atom and these facts agree with the Kapustinskii–Yatsimirskii formula discussed above. This regularity is clearly seen in Fig. 2 where the values of U^0 for $(R_pNH_{4-p})Cl$ (R = Me, Et, *n*-Pr, and *n*-Bu) are plotted against p (for $p = 0$ and 1 the appropriate values were taken from ref. 10). For the series of branched mono-alkanamine hydrochlorides studied the values of U^0 do not change significantly with the size of an alkanaminium cation. It is worth mentioning that a similar dependency has been also observed previously for unbranched derivatives [10]. Figure 2 shows that values of U^0 depend linearly on the number of alkyl substituents for a given R. Thus, applying an approximation procedure U^0 values for appropriate quaternary salts are obtained. They are listed in Table 8. "Thermochemical" radii exhibit expected trends against the structure of an alkanaminium cation. This quantity presents, however, only an empirical constant and does not provide direct information on the true dimensions of ions. None the less, this magnitude appears to be very helpful in the examination of crystal lattice energy problems and, as has been proved many times in the past, it can be used for the estimation of unknown crystal lattice energies [143–145].

Unexpected trends for $\Delta H^0_{f,c}$ and U^0 of *n*-Bu substituted alkanaminium chlorides (Fig. 2) make impossible the estimation of any of these quantities for $(n\text{-}Bu_4N)Cl$ in the manner described previously. Therefore, we made an effort to evaluate these characteristics using information from the literature. Conway et al. [17] derived the ionic radii for $n\text{-}Pr_4N^+$ and $n\text{-}Bu_4N^+$ being equal to 0.452 and 0.494 nm, respectively, on the basis of the bond length analysis. Assuming that "thermochemical" radii for these ions change proportionally to those given above values for r_K of $n\text{-}Bu_4N^+$ equal to 0.271 nm are obtained. Substituting this value in eqn. (12) gives U^0 for $(n\text{-}Bu_4N)Cl$ equal to 521 kJ mol^{-1}. This value seems to be very probable considering previously discussed trends of crystal lattice energies (Fig. 2). Great differences from the linearity observed for other compounds of the $(n\text{-}Bu_pNH_{4-p})Cl$ series requires, however, further examination.

Our present knowledge of the chemistry of quaternary alkanaminium salts reveals that R_4N^+ ions actually exist in the solid and liquid state. For better understanding of various thermochemical problems it is, however, necessary to know the thermochemical characteristics for these species in a hypothetical gaseous state. One of the most important quantities describing properties of these ions is the enthalpy of formation. This characteristic refers directly to the alkane cation affinity. To handle this problem let us consider two pathways for dissociation of alkanaminium ions [13]

$$R_pNH^+_{4-p(g)} \begin{array}{l} \nearrow R_pNH_{3-p(g)} + H^+_{(g)} \qquad PA[R_pNH_{3-p}] \qquad (13) \\ \searrow R_{p-1}NH_{4-p(g)} + R^+_{(g)} \qquad AKA[R_{p-1}NH_{4-p}] \qquad (14) \end{array}$$

Pathway (13) is available for ammonium and primary, secondary, and tertiary alkanaminium ions and the enthalpy change for this process is named proton affinity (*PA*). On the other hand, pathway (14) exist for all types of alkanaminium ions and the enthalpy for this process is named, by analogy, alkane cation affinity (A*KA*). Applying simple Hess's law to both above equations gives

$$\mathrm{A}KA\left[\mathrm{R}_{p-1}\mathrm{NH}_{4-p}\right] = \Delta H^0_{\mathrm{f,g}}\left[\mathrm{R}_{p-1}\mathrm{NH}_{4-p}\right] + \Delta H^0_{\mathrm{f,g}}[\mathrm{R}^+] + PA\left[\mathrm{R}_p\mathrm{NH}_{3-p}\right] - \Delta H^0_{\mathrm{f,g}}\left[\mathrm{R}_p\mathrm{NH}_{3-p}\right] - \Delta H^0_{\mathrm{f,g}}[\mathrm{H}^+] \qquad (15)$$

For the compounds of the series $\mathrm{R}_{p-1}\mathrm{NH}_{4-p}$ (R = Me, Et, *n*-Pr, *n*-Bu, and $p = 1, 2, 3$) the appropriate alkane cation affinities can be evaluated from the available literature data. Thus, taking previously mentioned values for $\Delta H^0_{\mathrm{f,g}}[\mathrm{H}^+]$, $PA[\mathrm{R}_p\mathrm{NH}_{3-p}]$ (Table 7, ref. 10), $\Delta H^0_{\mathrm{f,g}}[\mathrm{R}_{p-1}\mathrm{NH}_{4-p}]$ and $\Delta H^0_{\mathrm{f,g}}[\mathrm{R}_p\mathrm{NH}_{3-p}]$ (Table 7, footnotes at Table 3, $\Delta H^0_{\mathrm{f,g}}[n\text{-BuNH}_2] = -92.0$ [14,107]), and assuming for $\Delta H^0_{\mathrm{f,g}}[\mathrm{Me}^+]$, $\Delta H^0_{\mathrm{f,g}}[\mathrm{Et}^+]$, $\Delta H^0_{\mathrm{f,g}}[n\text{-Pr}^+]$, and $\Delta H^0_{\mathrm{f,g}}[n\text{-Bu}^+]$ values equal to (in kJ mol^{-1}) 1095, 917, 868, and 839 [146], respectively, we have derived appropriate alkane cation affinities. They are shown as points in Fig. 3. Of course, this procedure does not allow

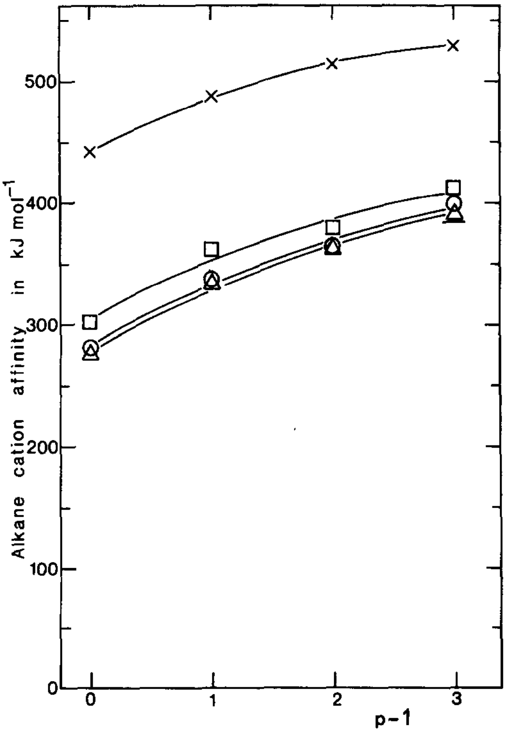

Fig. 3. Alkane (R) cation affinities for $\mathrm{R}_{p-1}\mathrm{NH}_{4-p}$: ×, R = Me; □, R = Et; ○, R = *n*-Pr; and △, R = *n*-Bu (△̲ denotes the extrapolated value).

evaluation of alkane cation affinities for tertiary amines. However, from a simple thermochemical cycle for quaternary salts

$$\begin{aligned} \mathrm{A}KA[\mathrm{R_3N}] &= \Delta H^0_{\mathrm{f,g}}[\mathrm{R_3N}] + \Delta H^0_{\mathrm{f,g}}[\mathrm{R^+}] + \Delta H^0_{\mathrm{f,g}}[\mathrm{Cl^-}] - \Delta H^0_{\mathrm{f,c}}[(\mathrm{R_4N})\mathrm{Cl}] \\ &\quad - U^0[(\mathrm{R_4N})\mathrm{Cl}] - 2RT \end{aligned} \tag{16}$$

Therefore, using appropriate values for $\Delta H^0_{\mathrm{f,g}}[\mathrm{R_3N}]$, $\Delta H^0_{\mathrm{f,c}}[(\mathrm{R_4N})\mathrm{Cl}]$, and $U^0[(\mathrm{R_4N})\mathrm{Cl}]$ listed in Tables 7 and 8 and previously indicated values for $\Delta H^0_{\mathrm{f,g}}[\mathrm{R^+}]$ and $\Delta H^0_{\mathrm{f,g}}[\mathrm{Cl^-}]$ we derived Me*KA*, Et*KA*, and *n*-Pr*KA* for $\mathrm{Me_3N}$, $\mathrm{Et_3N}$, and *n*-$\mathrm{Pr_3N}$, respectively. These values are shown as points in Fig. 3 (for $p - 1 = 3$). The derived alkane cation affinities for tertiary amines fit quite well with other values and this makes the standard enthalpies of formation and crystal lattice energies for quaternary salts estimated by extrapolation more realistic.

Alkane cation affinities for a given series of amines (R constant) can be satisfactorily approximated with a simple quadratic equation. Using a standard computer program we derived coefficients for this polynomial (Table 9). The points belonging to the solid lines in Fig. 3 correspond also to this equation. Examining the data indicates that curves for Et*KA* and *n*-Pr*KA* show almost the same curvature and that they are only shifted by a constant value equal to -21.5 kJ mol^{-1}. Assuming that the same tendency holds for *n*-Bu cation affinity we have estimated, from the available data, that the values of this quantity should be shifted by -4.5 kJ mol^{-1} against the appropriate values for *n*-Pr*KA* (Fig. 3). By extrapolation a value equal to 392 kJ mol^{-1} for *n*-Bu*KA* of *n*-$\mathrm{Bu_3N}$ (Table 9) was obtained. Combining this value with those for other quantities in eqn. (16) we have obtained a value of -534 kJ mol^{-1} for the standard enthalpy of formation of *N*,*N*,*N*-tributyl-1-butanaminium chloride (Table 8). Further, using the estimated values of $\Delta H^0_{\mathrm{f,c}}$ for quaternary chlorides (Table 8) true enthalpies of the thermal decomposition of these derivatives can be predicted from eqn. (2). These characteristics were calculated assuming appropriate values for the enthalpy of formation of amines and chloroalkanes (see Table 7, footnotes at Table 3, and $\Delta H^0_{\mathrm{f,g}}[n\text{-}\mathrm{C_4H_9Cl}] = -154.5$ kJ mol^{-1} [107]) (Table 8). The

TABLE 9

Alkane cation affinities of $\mathrm{R}_{p-1}\mathrm{NH}_{4-p}$ and enthalpies of formation for $\mathrm{R_4N^+}$ [a]

R	Polynomial approximating A*KA* (c.f. Fig. 3)	R*KA* of $\mathrm{R_3N}$ from the polynomial	$\Delta H^0_{\mathrm{f,g}}[\mathrm{R_4N^+}]$
Me	$-7.7(p-1)^2+51.5(p-1)+443.1$	529	542
Et	$-6.8(p-1)^2+55.2(p-1)+305.1$	409	415
n-Pr	$-5.9(p-1)^2+55.2(p-1)+283.7$	396	311
n-Bu	$-5.9(p-1)^2+55.2(p-1)+279.2$	392	225

[a] All values in kJ mol^{-1}.

comparison of these estimated enthalpies of the thermal dissociation with those derived from the thermogravimetric curves (Table 3) shows clearly that the latter exceed the expected ΔH_v values for the process from ca. 100 kJ mol^{-1}, in the case of (n-Bu$_4$N)Cl, to ca. 200 kJ mol^{-1}, for (Me$_4$N)Cl. These facts strongly support the concept of the existence of the kinetic barrier for the process.

Lastly, from eqn. (14)

$$\Delta H^0_{\mathrm{f,g}}\left[\mathrm{R}_p\mathrm{NH}^+_{4-p}\right] = \Delta H^0_{\mathrm{f,g}}\left[\mathrm{R}_{p-1}\mathrm{NH}_{4-p}\right] + \Delta H^0_{\mathrm{f,g}}\left[\mathrm{R}^+\right] - \mathrm{A}K\!A\left[\mathrm{R}_{p-1}\mathrm{NH}_{4-p}\right] \qquad (17)$$

Therefore, using the appropriate ancillary data from Tables 7 and 9, as well as values reported earlier in the text, we estimated standard enthalpies of formation of quaternary alkanaminium ions. They are shown in Table 9. These characteristics were not previously available.

6. *Final remarks*

The enthalpies of formation of crystalline alkanaminium chlorides derived in this and previous work [10] are slightly lower compared with those obtained by the calorimetric method. These differences may be due partially to the fact that the method applied is actually a non-equilibrium technique. Thus, the experimental P/P_0 values (equal to α) might be somewhat lower than those corresponding to the equilibrium conditions at a given temperature. An analogous effect can, however, also be caused by the imperfect behaviour of decomposition fragments in the gaseous phase. We discussed this issue earlier in the text and we believe that this is the main factor causing the observed discrepancies. On the other hand, the agreement can be considered as quite good, taking into account that both characteristics have been obtained by the application of totally different techniques.

The last question remaining is why the crystal lattice energy is affected only insignificantly by the size and structure of an alkanaminium cation. To explain this phenomenon factors influencing this quantity must be considered. As is well known, in the case of ionic crystals the crystal lattice energy is affected mainly by the coulombic interaction between charged centers. For the compounds studied here these centers are located on N and Cl and they are virtually the same. Therefore, nearly constant values of the crystal lattice energy might be obtained if the N–Cl distance was independent of the size of an alkyl substituent. This conclusion is fully supported by the results of crystallographic investigations. It has been found that the hydrogen bond $\geqslant$N–H $\cdots$ Cl, whose distance is affected only insignificantly by the attachment to nitrogen alkyl groups, plays an important role in the structure of alkanaminium chlorides [147–149]. Alkyl substituents which, of course, have much larger dimensions than N, H or Cl atoms are placed in the lattice in such a way that the distance between N and Cl is uninterrupted. Sometimes, they form chains [147] or layered structures [150]. Undoubtedly, these considerations would be strengthened by the calculation of crystal lattice energies using lattice parameters. We are currently working on this problem.

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