Thermochimica Acta, 68 (1983) 233–260
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL PROPERTIES OF AMINE HYDROCHLORIDES. PART I. THERMOLYSIS OF PRIMARY *n*-ALKYLAMMONIUM CHLORIDES

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(Received 5 April 1983)

ABSTRACT

Thermogravimetry and differential thermal analysis have been applied to the investigation of the thermal properties of primary *n*-alkylammonium chlorides of general formula $(C_nH_{2n+1}NH_3)Cl$, with $n = 0$–8. Irrespective of the chain-length, the thermolysis of amine hydrochlorides occurs in one step and leads to the total volatilization of the salts. The experimental TG and DTG curves were used for examination of the thermodynamics and kinetics of this process.

The values evaluated for the enthalpy of vaporization enable the estimation of some parameters characterizing this group of compounds, namely, the enthalpy of formation and the energy of the crystal lattice of the salts, as well as the enthalpy of formation of the $C_nH_{2n+1}NH_3^+$ ions.

The Jacobs and Russell-Jones equation, describing the kinetics of sublimation, has been adapted to the dynamic conditions. It was found that this equation approximates very well with the experimental TG data and evaluated values of the apparent activation energy are very close to the values of the enthalpy of volatilization. On the other hand, the standard kinetic treatment of the data indicated that two-dimensional diffusion (D2 mechanism) may govern the volatilization process.

The values of characteristic parameters describing the thermal properties of amine hydrochlorides, namely, temperature limits, enthalpy and kinetic constants of thermolysis, depend notably on the length of the aliphatic chain of the amine.

INTRODUCTION

Amine hydrochlorides are the simplest salt-like derivatives of amines. Hence, it is understandable that chemists have been interested in this group of compounds for a long time.

A number of properties of these compounds are known: comparison of these properties indicates that NH_4Cl occupies a distinct position among amine hydrochlorides. This mainly results from the specific properties and structure of NH_3. Since NH_4Cl is the simplest member of this group, it has been chosen most often as a model compound for investigations. Some aspects of the thermodynamics of thermolysis of amine hydrochlorides have

0040-6031/83/$03.00

been studied [1–15]; however, most works in this area concern NH_4Cl. Some attention has been devoted to the investigation of the kinetics of thermolysis of NH_4Cl [16–22], whereas this problem has not been studied in the case of other alkylammonium chlorides. The volatilization of alkylammonium chlorides is of special interest in studies of the mechanism of evaporation since the gasification process involves an endothermic dissociation reaction.

This paper reports fundamental thermodynamic and kinetic characteristics for several simple members of the mono-*n*-alkylammonium chloride series. Such data are of interest since: (i) they permit trends and variations in thermochemical and kinetic parameters within a closely related series of compounds to be observed; (ii) very little information is available on such characteristics of solid compounds of this type; (iii) thermochemical data, in conjuction with values of enthalpy of formation of amines and amine proton affinities, allow the calculation of the enthalpies of formation and the crystal lattice energies of amine hydrochlorides via a thermochemical cycle; and (iv) these data allow the evaluation of the enthalpies of formation of the $C_nH_{2n+1}NH_3^+$ ions.

EXPERIMENTAL

Ammonia (P.O.Ch.), methylamine (B.D.H.), ethylamine (Fluka AG, Buchs SG), *n*-propylamine (UCB, Belgium), *n*-butylamine (Loba, Austria), *n*-amylamine (B.D.H.), *n*-hexylamine (Fluka AG, Buchs SG), *n*-heptylamine (Koch-Light Lab.) and *n*-octylamine (Koch-Light Lab.) were all obtained as pure grade and used as received. Other reagents of analytical grade have been used throughout.

The amine hydrochlorides were synthesized by passing a stream of dried hydrogen chloride through a solution of the appropriate amine in anhydrous ethyl ether [23–26]. The resulting white precipitates were filtered and thoroughly washed several times with ice-cold ether. The compounds were dried in a vacuum desiccator over P_2O_5. They were checked for purity by determination of chloride ions and elementary analysis. None of the salts contained either free acid or base. The anhydrous, white salts were crystalline, non-hygroscopic and stable, at least up to their melting points.

The thermal analyses were carried out on an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen. The sample was placed on one platinum plate (see ref. 27, Fig. 3e). Other operating conditions were: mass of sample = 3×10^{-4} mole, heating rate = 4.9 ± 0.2 K min^{-1}, sensitivities of DTG, DTA and TG galvanometers = 1/10, 1/5 and 50 mg, respectively. The analyzed compounds were ground in an agate mortar and particles passing through a standard mesh (150 μm) were used for analyses.

Values of the degree of conversion (α) and corresponding values of

TABLE 1

Thermal decomposition of $[CH_3(CH_2)_5NH_3]Cl$
(See Ref. 29, Fig. 2A)

α	T (K)	$d\alpha/dt$ (min^{-1})
0.1	467.9	0.0195
0.2	483.4	0.0405
0.3	492.5	0.0586
0.4	499.0	0.0765
0.5	504.2	0.0967
0.6	509.1	0.112
0.7	513.4	0.120
0.8	517.8	0.132

temperature (T) and rate of weight loss ($d\alpha/dt$) were determined using experimental curves in a manner described previously [28,29]. For each compound, the set of experimental data points, used in further calculations, was taken as a mean from at least 3 replicate measurements. An example of the set of data points is given in Table 1.

All calculations were performed on a TI 59 calculator.

RESULTS

Mono-*n*-alkylammonium chlorides of general formula $(C_nH_{2n+1}NH_3)Cl$, with $n = 0$–8, undergo various thermal transformations upon heating to 700 K. The thermal analysis run recorded by a derivatograph for $[CH_3(CH_2)_5NH_3]Cl$ and presented in our previous report (ref. 29, Fig. 2A) is typical for all the compounds investigated. The essential parameters characterizing the thermal behaviour of this group of compounds, derived from thermal analysis curves, are compiled in Table 2 together with the available literature data.

It is well-known that ammonium and mono-*n*-alkylammonium chlorides undergo a number of phase transitions. The different known phases are referred to as phases I, II, III and so on, in order of the decreasing temperatures. These polymorphic transformations lead to crystal structures of higher symmetries with increasing temperature.

A relatively great amount of attention has been devoted to the investigation of polymorphic transformations of NH_4Cl. The transition $II \rightarrow I$ for this compound appears just before the onset of sublimation (Table 2) and the temperature of this process may depend on experimental conditions [36]. Phase I of NH_4Cl admits the tetragonal structure of the NaCl crystal (space group O_h^5), while phase II has a monoclinic structure of the CsCl-type (space group O_h^1) [34].

TABLE 2

The thermal analyses of mono-*n*-alkylammonium chlorides $(C_nH_{2n+1}NH_3)Cl$

Substance $(C_nH_{2n+1}NH_3)Cl$ n	Sample weight (mg)	Peak temperature [a] (K)						Temperature [a] (K)			Parameters describing the beginning of the second stage	
		DTG	DTA					$T_{0.1}$	$T_{0.8}$	$\Delta T_\alpha = T_{0.8} - T_{0.1}$		
			T_σ		T_m		T_p					
			This work	From literature	This work	From literature					α	T (K)
0	18.8	507	467	457.5 [5,31,32] 457.7 [33,34] 458 [35] 458.2 [9] 459.5 [8] 453–468 [36]			510	456.9	509.1	52.2	0.93	517
1	22.3	521			509	498 [10] 498–499 [37] 499 [31] 500–501 [32] 506 [24] 505–506.5 [38]	523	463.5	522.6	59.1	0.91	526

2	25.5	511	360	345 [39]	381	381 [24] 382 [40] 383 [41] 382–383 [10,37]	511	454.7	509.7	55.0	0.90	517
3	28.3	502	407	408 [24]	435	428–431 [42] 439 [24]	504	450.7	502.1	51.4	0.87	507
4	30.9	503			483	468 [43] 487 [24] 488 [44] 489 [10]	506	456.0	505.4	49.4	0.84	508
5	32.2	505			499	502 [24]	507	458.3	507.6	49.3	0.85	513
6	35.3	513			495	489–491 [23] 492 [45] 493 [24] 494 [46]	516	467.9	517.8	49.9	0.86	522
7	37.2	516		303 [24]	480	474–477 [23] 479 [46] 480 [24] 515–518 [37]	520	470.4	522.0	51.6	0.87	530
8	39.0	517		305, 308, 313 [24]	468	468–470 [23] 471 [47] 472 [46] 477 [24]	521	471.3	522.3	51.0	0.88	529

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[a] The symbols were taken from ref. 30. T_p = temperature of the peak, T_σ = temperature of a solid-state phase transition, T_m = temperature of melting and T_α = temperature at which the degree of conversion is equal to α (i.e. $T_{0.1} = T_{\alpha=0.1}$).

A number of phase transitions have been observed for all compounds of the homologous series examined in this work [24,39]. For most compounds, however, polymorphic transformations appear below room temperature and, therefore, they could not be observed in our experiments. It may also be seen in Table 2 that the transition temperatures which were derived in this work agree fairly well with those reported in the literature.

All the alkylammonium chlorides investigated undergo fusion as shown in Table 2. For some compounds, melting occurred before the onset of thermal decomposition; for others, melting occurred simultaneously with thermal decomposition [24]. The melting temperatures show an initial sharp decrease, from $n = 1$ to $n = 2$, then they increase to a maximum for *n*-amylammonium chloride, followed by a gradual decrease.

Heating *n*-alkylammonium chlorides above their melting points caused thermal processes which led to a total volatilization of the salts. These processes involve the transfer of the substance from the liquid to the gas phase and, therefore, they may be considered as vaporization. In contrast, in the case of NH_4Cl this is sublimation, since the process occurs from the solid phase.

Thermogravimetric curves for all the compounds investigated show a two-stage course for the volatilization (see ref. 29, Fig. 2A and Table 2). The first fast step, in which up to 85% of the sample leaves the system, is followed by a slow one, seen as a "tail" on TG curves, in which the remaining part of the sample disappears. In further calculations only the first step will be considered. Our thermogravimetric results are similar to those obtained by Gutmann and Kertes [25] for higher alkylammonium chlorides. However, contrary to the above authors, we did not observe thermal destruction of the organic parts of molecules, at least in the solid phase.

The characteristic temperatures, namely, T_p (from DTG and DTA curves), $T_{0.1}$ and $T_{0.8}$, show dependence on the length of the aliphatic chain of the amine. Initially, an increase in the values of the characteristic temperatures is observed, moving from $n = 0$ to $n = 1$, then they decrease to a minimum for *n*-propylammonium chloride, followed by a gradual increase. ΔT_α values show similar regularities, however, the position of the minimum is different compared with the other parameters mentioned and the changes are less distinct. Also, the characteristic parameters describing the beginning of the second stage, as listed in Table 2, show similar dependencies.

DISCUSSION

General nature of the volatilization process

Although thermal decomposition and sublimation of ammonium chloride has been studied extensively in the past, there is still no clear picture of the chemical processes which take place. The early works concerned with this problem [1–5] revealed that NH_4Cl is completely dissociated to NH_3 and HCl in the vapor phase. This opinion was confirmed later by thermochemical calculations (see refs. in Table 3), as well as recently by theoretical considerations [48,49]. Generally, alkylammonium chlorides should show similar behaviour during the vaporization process [10–13], although recent theoretical calculations indicate that interactions between amines and HCl in the vapor phase may be stronger [50].

Therefore, using the foregoing considerations, as well as experimental facts, the volatilization of alkylammonium chlorides can be described by the equation

$$(C_nH_{2n+1}NH_3)Cl_{(s,l)} \rightarrow C_nH_{2n+1}NH_{2(g)} + HCl_{(g)} \qquad (1)$$

The relevant literature data indicate that evaporation of these compounds proceeds above the boiling points for the appropriate amines [51]. Hence, they should always appear, together with HCl, in the gas phase.

The mechanism of the volatilization of ammonium salts is still a matter of controversy [52]. In the sublimation of NH_4Cl, presumably at least three stages are involved [17,19,21,22]: these references indicate that the mechanism of sublimation which best accounts for the experimental facts can be presented by the scheme

$$\begin{array}{ccccccc} NH_4^+Cl^- & \rightleftharpoons & NH_3\text{-}H\text{-}Cl & \rightleftharpoons & NH_3\ldots H\text{-}Cl(a) & \rightleftharpoons & NH_3(a)+HCl(a) \\ \underline{\text{I}} & & \underline{\text{II}} & & \underline{\text{III}} & & \upharpoonleft\downharpoonright \\ & & & & & & NH_3(g)+HCl(g) \end{array} \qquad (2)$$

I represents an ammonium chloride ion-pair at a half-crystal site [19,53,54]. Sublimation commences by the transfer of a proton from NH_4^+ to Cl^-, and II represents the transition state. When proton transfer is complete (III), the NH_3 and HCl molecules no longer have coulombic interactions with the rest of the lattice which held the ions in position and are thus free to migrate over the surface of the crystal as a mobile adsorbed phase. The migration of the adsorbed molecules over the surface followed by their diffusion through the gas phase represents the sublimation process.

Because numerous similarities have been observed between NH_4Cl and alkylammonium chlorides, it may be assumed that the mechanism of evaporation of these compounds is the same.

Thermodynamics of evaporation

The enthalpy of volatilization was evaluated using an approximate method as proposed by Stepin et al. [55]. The volatilization of 1 mole of alkylammonium chloride results in the formation of 2 moles of gaseous products [eqn. (1)]. Hence, based on our previous considerations [28], the heat of vaporization (ΔH_v), or sublimation (ΔH_s), can be estimated from the equation

$$\ln \alpha = -\frac{\Delta H_v}{2RT} + \text{const.} \tag{3}$$

A similar approach has recently been applied for the determination of the enthalpy of evaporation of several pure substances and aqueous solutions of inorganic salts [56].

TABLE 3

Enthalpies of evaporation of mono-*n*-alkylammonium chlorides [a]

Substance $(C_nH_{2n+1}NH_3)Cl$ n	Const.	ΔH_v (kJ mole^{-1})	ΔH_s (kJ mole^{-1})	Enthalpy of volatilization (kJ mole^{-1})	
				From literature [b]	Calculated using the standard enthalpy of formation at 298 K [d]
0	18.4		156.8	158.2 (693–773) [c]	177.0 *
				156.5 (613) [c]	175.9 **
				165.3 (573) [c]	
				173.3 (533) [c]	
				183.7 (493) [c]	
				158.2 (518–618) [c]	
				165.7 [2]	
				164 (446–494) [4]	
				175.4 (291), 171.3 (> 457.5) [5]	
				176.4, 176.9 (298.1) [6]	
				177.0 (298) [7]	
				160.7 (503–611) [8]	
				160 (391–494) [16]	
				164.9 [21]	
1	16.3	143.4		114.3 (497–593) [10]	165.6 *
				189.5 (502–690) [14]	178.0 **
2	17.3	148.0		34.3 (382–480) [10]	
3	18.3	154.4			
4	19.2	163.0		61.9 (489–508) [10]	
				206.0 (488–724) [14]	
5	19.4	165.6			
6	19.6	170.0			
7	18.8	165.2			
8	19.2	168.7			

[a] Values of ΔH_v, ΔH_s and const. were calculated from eqn. (3), within a range of α from 0.1 to 0.8. The linear correlation coefficient was always better than 0.9995.

[b] The temperature range, in K, is given in parentheses.

[c] Values from the works reviewed in ref. 1.

[d] Values used in the calculations (kJ mole^{-1}): $\Delta H^0_{f,g}[HCl] = -92.3$ [51] *,**; $\Delta H^0_{f,g}[NH_3] = -46.2$ [51] *,**; $\Delta H^0_{f,g}[CH_3NH_2] = -28.0$ [51] *,**; $\Delta H^0_{f,c}[NH_4Cl] = -315.5$ [51] * and -314.4 [12] **; $\Delta H^0_{f,c}[(CH_3NH_3)]Cl = -285.9$ [51] * and -298.3 [12] **.

The values evaluated for the enthalpy of volatilization are listed in Table 3. A relatively great amount of attention has been devoted to the evaluation of the enthalpy of sublimation of NH_4Cl, although, the data available are scattered. The value of ΔH_s derived by us is in good agreement with those evaluated from the DTA technique [8,21]. The information reported in the literature concerning sublimation of alkylammonium chlorides is fragmentary. Moreover, the available data on ΔH_v are so scattered that any reliable comparison of our ΔH_v values with the literature values could not be performed.

Kinetics of volatilization

Classical description

From the formal point of view, the process of volatilization of alkylammonium chlorides can be considered as a chemical reaction resulting in mass loss of the sample. Therefore, a typical treatment may be applied to the examination of the kinetics of this process. The methods of evaluating kinetic constants have been described in our previous work [29]. An example of the full set of kinetic calculations for the evaporation of *n*-hexylammonium chloride, is given in Table 4. Qualitatively comparable results were obtained for the other compounds in the homologous series, thus any conclusions drawn are proper for all the compounds investigated.

In searching for an adequate form of the integral or differential equation, we compared values of the correlation coefficient and the δ function. According to statistical rules, the higher the values of $|r|$ and the lower the values of δ, the better the approximation formula is for a given function $g(\alpha)$ or $f(\alpha)$ [28,29]. Of course, both functions should describe the same reaction mechanism. Reviewing the data compiled in Table 4, it is noticed that the D2 mechanism is the most satisfactory for the foregoing requirements, since: (i) methods A and B show the highest values of $|r|$, (ii) values of δ are relatively low, and (iii) values of δ are similar for integral and differential methods. The values derived for the activation energy, having physical meaning, should not be much lower than the value for the enthalpy change of a given process. For these reasons, the functions $g(\alpha)$ and $f(\alpha)$, corresponding to the mechanisms P1, P2, P3, P4, A2 and A3, have been excluded from the considerations. It may be seen in Table 4 that the $g(\alpha)$ function corresponding to the R1 mechanism gives a very good fit to the experimental data, however, this is not observed for the $f(\alpha)$ function. It is worth mentioning that the zero-kinetic-order equation (Polanyi–Wigner mechanism [57]) has been used in the description of the kinetics of vacuum sublimation of NH_4Cl [16–18]. Special attention should be devoted to the R2 mechanism, since the $g(\alpha)$ function corresponding to this has been found to describe satisfactorily the kinetics of isothermal sublimation of some ammonium salts under atmospheric pressure [53,54]. This function has also

TABLE 4

Kinetic constants for volatilization of $[CH_3(CH_2)_5NH_3]Cl$ (classical description)

Symbol of the mechanism [c]	Method of evaluation of kinetic constants [a]											
	A: eqn. (8) in ref. 29			B: eqn. (9) in ref. 29			C: eqn. (10) in ref. 29			D [b]: eqn. (11) in ref. 29		
	E	*Z*	|*r*|	*E*	*Z*	|*r*|	*E*	*Z*	δ	*E*	*Z*	δ
R1	7.70 4	1.39 05	0.99948	8.11 4	2.00 04	0.99955	7.71 4	1.41 05	0.019038	7.74 4	1.68 05	0.018997
R2	8.85 4	1.48 06	0.99924	9.26 4	1.86 05	0.99928	8.84 4	1.44 06	0.026727	8.87 4	1.70 06	0.026797
R3	9.27 4	3.01 06	0.99843	9.68 4	3.61 05	0.99853	9.26 4	2.94 06	0.040316	9.29 4	3.44 06	0.040385
P1	5.57 4	7.45 02	0.99943	5.98 4	1.49 02	0.99953	5.58 4	7.58 02	0.014439	5.62 4	9.58 02	0.014379
P2	4.86 4	1.27 02	0.99941	5.27 4	2.90 01	0.99952	4.87 4	1.29 02	0.012905	4.92 4	1.71 02	0.012837
P3	3.44 4	3.42 00	0.99931	3.85 4	1.11 00	0.99948	3.44 4	3.39 00	0.0098307	3.51 4	4.99 00	0.0097441
E1							−9.84 4	1.45 −13	0.20601	−9.88 4	1.20 −13	0.20610
B1							8.23 4	−2.06 06	−2.0287	8.26 4	−2.44 06	−2.0288
P4	1.31 4	9.68 −03	0.99867	1.72 4	8.21 −03	0.99931	1.31 4	9.62 −03	0.0052290	1.43 4	2.09 −02	0.0050862
F1	1.02 5	9.67 07	0.99582	1.06 5	1.06 07	0.99609	1.01 5	8.21 07	0.073267	1.02 5	1.14 08	0.073253
A2	4.67 4	1.07 02	0.99520	5.08 4	2.54 01	0.99582	4.67 4	1.06 02	0.035788	4.72 4	1.40 02	0.035904
A3	2.84 4	8.69 −01	0.99439	3.25 4	3.40 −01	0.99553	2.84 4	8.62 −01	0.023464	2.92 4	1.35 00	0.023621
D1	1.62 5	9.60 13	0.99955	1.66 5	6.59 12	0.99957	1.62 5	9.00 13	0.037496	1.63 5	1.21 14	0.037422
D2	1.77 5	2.01 15	0.99972	1.81 5	1.27 14	0.99972	1.76 5	1.75 15	0.032128	1.77 5	2.34 15	0.032164
D3	1.94 5	3.72 16	0.99853	1.98 5	2.14 15	0.99857	1.93 5	3.23 16	0.082017	1.93 5	3.37 16	0.082077
D4	1.82 5	1.93 15	0.99948	1.86 5	1.18 14	0.99949	1.82 5	1.84 15	0.045273	1.82 5	1.92 15	0.045307

TABLE 4 (continued)

Symbol of the mechanism	Method of evaluation of kinetic constants [a]								
	E: eqn. (12) in ref. 29			F: eqn (13) in ref. 29			G: eqn. (14) in ref. 29		
	E	Z	δ	E	Z	δ	E	Z	δ
R1	8.12 4	2.04 04	0.018771	7.91 4	2.34 05	0.057642	8.30 4	2.85 04	0.057283
R2	9.25 4	1.82 05	0.027200	1.07 5	1.40 08	0.055303	1.11 5	1.33 07	0.055754
R3	9.67 4	3.54 05	0.040809	1.16 5	9.28 08	0.090997	1.20 5	8.13 07	0.091447
P1	5.99 4	1.52 02	0.014167	5.78 4	1.30 03	0.053910	6.16 4	2.06 02	0.053553
P2	5.27 4	2.89 01	0.012628	5.06 4	2.21 02	0.052691	5.44 4	2.91 01	0.052339
P3	3.85 4	1.10 00	0.0095466	3.64 4	6.31 00	0.050300	4.01 4	1.44 00	0.049960
E1	−9.42 4	−1.68 −14	−0.20560	−6.34 3	6.75 −04	0.043593	0.00 0	3.13 −03	0.064105
B1	8.64 4	−2.80 05	−2.0293	5.05 4	1.27 03	0.18228	5.43 4	2.25 02	0.18272
P4	1.72 4	8.19 −03	0.0049213	1.50 4	2.29 −02	0.046848	1.84 4	9.57 −03	0.046567
F1	1.06 5	1.13 07	0.073754	1.35 5	2.49 11	0.16655	1.39 5	2.66 10	0.16703
A2	5.08 4	2.52 01	0.036282	8.03 4	4.40 05	0.12828	8.42 4	5.30 04	0.12873
A3	3.25 4	3.38 −01	0.023954	6.20 4	3.93 03	0.11574	6.59 4	5.97 02	0.11617
D1	1.67 5	7.70 12	0.037249	1.65 4	1.81 14	0.073402	1.69 5	1.14 13	0.073056
D2	1.81 5	1.38 14	0.032555	1.89 5	4.11 16	0.034894	1.93 5	2.27 15	0.035188
D3	1.97 5	1.82 15	0.082525	2.36 5	1.43 21	0.20841	2.40 5	6.39 19	0.20890
D4	1.86 5	1.10 14	0.045719	1.98 5	9.06 16	0.062009	2.02 5	4.79 15	0.062461

[a] Values are presented in computer notation, e.g. $-5.00-05 = -5.00 \times 10^{-5}$. E = apparent activation energy (J mole^{-1}), Z = constant (s^{-1}); $|r|$ = correlation coefficient; δ represents values of the statistical function given by eqn (15) in ref 29.

[b] Values of the p(x) function were calculated using the 10 truncated parts of the Legendre series [ref. 58, eqn. (18)].

[c] Ref. 28, Table 1.

TABLE 5

Kinetic parameters for evaporation of mono-*n*-alkylammonium chlorides (classical description)

Substance $(C_nH_{2n+1}NH_3)Cl$ *n*	Symbol of the mechanism [b]	Method of evaluation of kinetic constants [a]							
		C: ref. 29, eqn. (10)		E: ref. 29, eqn. (12)		F: ref. 29, eqn. (13)		G: ref. 29, eqn. (14)	
		E	*Z*	*E*	*Z*	*E*	*Z*	*E*	*Z*
0	R1	7.05 04	3.84 04	7.45 04	5.93 03	6.69 04	1.57 04	7.07 04	2.18 03
	R2	8.09 04	3.33 05	8.49 04	4.48 04	9.24 04	5.96 06	9.63 04	6.30 05
	D2	1.62 05	1.25 14	1.66 05	8.43 12	1.68 05	5.37 14	1.72 05	3.22 13
1	R1	6.35 04	4.10 03	6.76 04	7.20 02	7.25 04	3.86 04	7.64 04	5.10 03
	R2	7.29 04	2.64 04	7.70 04	4.04 03	9.53 04	6.63 06	9.92 04	6.82 05
	D2	1.47 05	1.17 12	1.51 05	8.67 10	1.64 05	7.39 13	1.68 05	4.67 12
2	R1	6.60 04	1.20 04	7.00 04	1.98 03	6.96 04	2.94 04	7.34 04	3.93 03
	R2	7.58 04	9.01 04	7.98 04	1.29 04	9.36 04	7.72 06	9.74 04	7.88 05
	D2	1.52 05	1.03 13	1.56 05	7.36 11	1.65 05	2.51 14	1.69 05	1.58 13
3	R1	6.93 04	3.50 04	7.32 04	5.37 03	7.95 04	4.51 05	8.33 04	5.35 04
	R2	7.93 04	2.83 04	8 33 04	3.88 04	1.04 05	1.44 08	1.08 05	1.40 07

	D2	1.59 05	9.51 13	1.63 05	6.51 12	1.78 05	1.08 16	1.82 05	6.32 14
4	R1	7.36 04	9.36 04	7.75 04	1.35 04	7.89 04	3.40 05	8.27 04	4.06 04
	R2	8.44 04	9.06 05	8.84 04	1.17 05	1.05 05	1.54 08	1.09 05	1.48 07
	D2	1.69 05	8.83 14	1.73 05	5.68 13	1.83 05	2.71 16	1.87 05	1.55 15
5	R1	7.48 04	1.16 05	7.88 04	1.69 04	7.65 04	1.79 05	8.03 04	2.19 04
	R2	8.57 04	1.14 06	8.97 04	1.45 05	1.03 05	8.69 07	1.07 05	8.51 06
	D2	1.71 05	1.19 15	1.75 05	7.56 13	1.83 05	2.29 16	1.87 05	1.30 15
6	R1	7.71 04	1.41 05	8.12 04	2.04 04	7.91 04	2.34 05	8.30 04	2.85 04
	R2	8.84 04	1.44 06	9.25 04	1.82 05	1.07 05	1.40 08	1.11 05	1.33 07
	D2	1.76 05	1.75 15	1.81 05	1.38 14	1.89 05	4.11 16	1.93 05	2.27 15
7	R1	7.56 04	8.35 04	7.97 04	1.23 04	7.69 04	1.19 05	8.09 04	1.52 04
	R2	8.68 04	8.22 05	9.10 04	1.08 05	1.04 05	5.60 07	1.08 05	5.43 06
	D2	1.73 05	6.15 14	1.78 05	4.92 13	1.84 05	8.83 15	1.88 05	5.01 14
8	R1	7.61 04	9.31 04	8.03 04	1.40 04	7.86 04	1.89 05	8.25 04	2.32 04
	R2	8.74 04	9.35 05	9.15 04	1.19 05	1.05 05	7.65 07	1.09 05	7.36 06
	D2	1.75 05	9.64 14	1.79 05	6.00 13	1.87 05	2.04 16	1.91 05	1.14 15

---

[a] Values are presented in computer notation, e.g., $-5.00-05 = -5.00 \times 10^{-5}$. E = apparent activation energy (J mole^{-1}); Z = constant (s^{-1}).

[b] Ref. 28, Table 1.

been applied by Naumova et al. [21] in the description of both isothermal and non-isothermal kinetics of sublimation of NH_4Cl under atmospheric pressure. Indeed, the R2 mechanism also gives a fairly good fit to the experimental data in our investigations.

The selected values of the kinetic constants for all the compounds investigated are listed in Table 5. The general trends are analogous to those observed for the enthalpy of evaporation.

Based on the Jacobs and Russell-Jones model

For the description of the rate of dissociative sublimation of ammonium salts, Jacobs and Russell-Jones [54] adopted a model which considers the volatilization process as a diffusional transfer of molecules from the solid to the vapor phase. Using this model, they developed an equation which can be presented in the differential form, i.e.

$$-\frac{\mathrm{d}N}{\mathrm{d}t}=\frac{4\pi D a n_0}{(D/a\beta\nu)+a/(a+\Delta)} \tag{4}$$

In the derivation of eqn. (4), it was assumed that sublimation takes place from the surface of the particles having spherical shapes. Thus, a represents the radius of the particle at the given fraction reacted, α, whereas a_0 denotes the initial radius corresponding to $\alpha = 0$. In eqn. (4), D is the coefficient of mutual diffusion [54], such that

$$D=\frac{3}{8\sigma^2(n_1+n)}\left(\frac{RT}{2\pi\mu}\right)^{1/2} \tag{5}$$

N is the number of molecules in the pellet of the solid substance; N_0 denotes the initial number of molecules in the pellet; n_0 is the concentration of the subliming species in the gas phase in equilibrium with the solid; n represents the concentration of the subliming species at a distance r from the center of the pellet; n_1 is the concentration of inert gas; β represents the evaporation coefficient; $\nu = \bar{c}/4$ (where $\bar{c}$ is the mean velocity of the subliming molecules in the vapor phase), Δ is the distance between collisions (i.e. a molecule after leaving the condensed phase travels a distance Δ before a collision occurs); σ is the mean diameter of the diffunding species and μ represents the reduced mass.

$$\frac{N}{N_0}=\frac{a^3}{a_0^3}=1-\alpha \tag{6}$$

and

$$-\frac{\mathrm{d}N}{\mathrm{d}t}=N_0\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{7}$$

Introducing eqns. (6) and (7) into eqn. (4), we obtain a differential form describing the rate of the sublimation process in isothermal conditions, i.e.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\frac{4\pi D n_0 a_0/N_0}{\left[D/(1-\alpha)^{2/3}a_0\beta\nu\right]+1/\left[(1-\alpha)^{1/3}+\Delta/a_0\right]} \tag{8}$$

In experimental conditions $n_1 \gg n$ [in eqn. (5)] and since $n_1 = P/RT$ (P = const., atmospheric pressure), $D \propto T^{3/2}$. From the kinetic theory of gases, $\nu \propto T^{1/2}$. As was mentioned earlier, n_0 represents the concentration of the subliming species (i.e. n-alkylamines or HCl) in equilibrium with the solid. Thus

$$n_0 = p_0/RT \tag{9}$$

where p_0 may be expressed by the Clausius–Clapeyron relationship

$$\ln p_0 = \frac{-\Delta H_\mathrm{v}}{2RT} + \mathrm{const.} \tag{10}$$

In non-equilibrium conditions, the partial pressure of the subliming species (p) is always lower than p_0: this may result from the fact that the process requires an activation energy such that $E > \Delta H_\mathrm{v}$. It may be assumed that the remaining parameters in eqn. (8), i.e. a_0, N_0, β and Δ do not depend on temperature. Therefore, introducing the foregoing relationships into eqn. (8) and making the necessary rearrangements we obtain

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}+\frac{X_1 T^{1/2}\,\mathrm{e}^{-E/2RT}}{\left[X_2 T/(1-\alpha)^{2/3}\right]+1/\left[(1-\alpha)^{1/3}+\Delta/a_0\right]} \tag{11}$$

where X_1 and X_2 are constants.

In isothermal conditions, eqn. (11) can be integrated by elementary methods [54] to give

$$\left(X_2 T-\frac{\Delta}{a_0}\right)\left[1-(1-\alpha)^{1/3}\right]+\tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]$$
$$-\left(\frac{\Delta}{a_0}\right)^2 \ln\left[\frac{(1-\alpha)^{1/3}+\Delta/a_0}{1+\Delta/a_0}\right]=\tfrac{1}{3}X_1 T^{1/2}\,\mathrm{e}^{-E/2RT}t \tag{12}$$

This integral equation has been applied successfully by Jacobs and Russell-Jones for description of the kinetics of sublimation of ammonium perchlorate.

In non-isothermal conditions, the rate of sublimation can be expressed as [59]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\left(\frac{\partial\alpha}{\partial T}\right)_t\frac{\mathrm{d}T}{\mathrm{d}t}+\left(\frac{\partial\alpha}{\partial t}\right)_T \tag{13}$$

Our further considerations will be limited to conditions of linear temperature increase, wherein $\mathrm{d}T/\mathrm{d}t = \Phi$ (heating rate). For the partial derivative $(\partial\alpha/\partial t)_T$, we may substitute the relationship given by eqn. (11). The functional dependence of the fraction reacted on temperature is not generally known. However, if we assume that this dependence results from the kinetic relationship for isothermal conditions, i.e. from eqn. (12), we obtain

$$\left(\frac{\partial \alpha}{\partial T}\right)_t = \frac{\frac{1}{2}X_1\left[T^{-1/2}\,\mathrm{e}^{-E/2RT} + \left(E/RT^{3/2}\right)\mathrm{e}^{-E/2RT}\right]t - 3X_2\left[1-(1-\alpha)^{1/3}\right]}{\left[X_2T/(1-\alpha)^{2/3}\right] + 1/\left[(1-\alpha)^{1/3} + \Delta/a_0\right]} \qquad (14)$$

Substitution of eqns. (11) and (14) into eqn. (13) leads to the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{\frac{1}{2}(X_1/\Phi)\left[3T^{1/2}\,\mathrm{e}^{-E/2RT} + \left(E/RT^{1/2}\right)\mathrm{e}^{-E/2RT}\right] - 3X_2\left[1-(1-\alpha)^{1/3}\right]}{\left[X_2T/(1-\alpha)^{2/3}\right] + 1/\left[(1-\alpha)^{1/3} + \Delta/a_o\right]} \qquad (15)$$

where $t = T/\Phi$ [59].

Integration of eqn. (15) [54,59] leads to the final form which describes the kinetics of sublimation under conditions of linear temperature increase, i.e.

$$\left(X_2T - \frac{\Delta}{a_0}\right)\left[1-(1-\alpha)^{1/3}\right] + \tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right] - \left(\frac{\Delta}{a_o}\right)^2 \ln\left[\frac{(1-\alpha)^{1/3} + \Delta/a_0}{1+\Delta/a_0}\right] = \frac{1}{3}\frac{X_1}{\Phi}T^{3/2}\,\mathrm{e}^{-E/2RT} \qquad (16)$$

X_2, X_1 and E are the characteristic parameters of sublimation and one may assume that they remain constant during the course of the process. In contrast, Δ/a_0 cannot be considered as a constant parameter: its value depends on the pressure [54] and also on the dimensions of the grain of the subliming species [60]. At moderate pressures of a foreign gas, $P \simeq$ atmospheric pressure, $\Delta \ll a_0$, and the influence of this parameter on the kinetics of sublimation is negligibly small. Then, eqn. (16) admits the form

$$X_2T\left[1-(1-\alpha)^{1/3}\right] + \tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right] = \frac{1}{3}\frac{X_1}{\Phi}T^{3/2}\,\mathrm{e}^{-E/2RT} \qquad (17)$$

Equation (17) is not amenable to testing by plotting some simple function of α against T. Therefore, the values of X_1, X_2 and E, giving the best fit of the experimental data to the equation were found using the standard least-squares criterion (Appendix A).

Values of characteristic constants for the evaporation process are listed in Table 6. As was shown earlier, both X_1 and X_2 contain some physical parameters and constants. Their meaning was not, however, defined precisely. Although all parameters should be positive this is not observed in the case of X_2. Thus, we cannot ascribe any physical significance to X_1 or X_2: they should be considered as mathematical constants. Instead, E may be considered as a parameter describing the dependence of reaction rate on temperature, i.e. as the activation energy.

TABLE 6

Kinetic constants for evaporation of primary *n*-alkylammonium chlorides (from the Jacobs and Russell-Jones model)

Substance $(C_nH_{2n+1}NH_3)Cl$ n	E (kJ mole^{-1})	X_1 (K$^{-1/2}$ s^{-1})	X_2 (K^{-1})
0	160	1170	2.72×10^{-5}
1	137	30.5	-5.46×10^{-4}
2	152	439	2.68×10^{-5}
3	151	328	-5.73×10^{-4}
4	158	711	-5.04×10^{-4}
5	166	1907	-3.55×10^{-4}
6	178	7082	1.28×10^{-4}
7	165	1096	-1.60×10^{-4}
8	171	2310	-6.39×10^{-5}

Values of E derived from eqn. (17) are very close to the values of the activation energy obtained from the integral equation corresponding to the D2 mechanism (Table 5). The observed differences are within the range of experimental uncertainties. This agreement may not be accidental. It was shown earlier that both methods are based on the same assumption, namely, that diffusion processes determine kinetics of vaporization of solid and liquid substances. The importance of surface diffusion in evaporation of other ammonium salts has been confirmed [54].

Equation (17) presents the simpler form of eqn. (16) in which the parameter Δ/a_0 is neglected. However, as the geometric surface area of the condensed phase decreases, a_0 approaches Δ in magnitude. Then, the rate of sublimation will decrease [53,60], since both terms containing Δ/a_0 in eqn. (16), are negative. Indeed, this effect was observed at the end of the vaporization process for all the compounds investigated (ref. 29, Fig. 2A). Gutmann and Kertes [25] observed a similar phenomenon for some long-chain alkylammonium chlorides: they ascribed the effect to the volatilization of carbonization products. This version does not seem to be very reliable, since volatilization of such products usually proceeds at higher temperatures.

Naumova et al. [21], starting from the expression derived by Jacobs and Russell-Jones [54] [eqn. (12)] and making many assumptions and approximations, also obtained a relationship describing the kinetics of sublimation under non-isothermal conditions. The form of this equation was analogous to the one describing phase boundary processes of cylindrical symmetry, R2 mechanism [28]. Although the authors obtained a fairly good fit of the proposed expression to the experimental data, nevertheless, in our opinion this approach seems to have many uncertain points. Using standard calculation techniques, Naumova et al. evaluated E to be 7.7×10^4 J mole^{-1} for the sublimation of NH_4Cl; this value is lower than that derived by us for the R2 mechanism (Table 5).

EVALUATION OF SOME IMPORTANT THERMOCHEMICAL CHARACTERISTICS

Many thermochemical quantities for ionic crystals can be derived from a simple Hess's law. The various relations between the quantities used can be presented in the form of a thermochemical cycle which is usually referred to as the Born–Fajans–Haber cycle. Figure 1 presents the cycle in a form convenient for calculation of the thermochemical characteristics [63,64] of interest to us.

In the cycle presented in Fig. 1, all magnitudes refer to 298 K and 1 atm. The meanings of the other symbols [63] are listed: ΔH_f denotes the enthalpy of formation of a given substance; $U + 2RT$ is the lattice enthalpy; U represents the lattice energy; I_H is the ionization potential of hydrogen; A_{Cl} denotes the electron affinity of Cl; PA represents the proton affinity of amine; and ΔH_s represents the enthalpy of sublimation.

Enthalpy of sublimation at 298 K

The values for the enthalpy of volatilization which were derived in this work do not refer to 298 K. Therefore, it was necessary to modify them according to the equation

$$\Delta H^0_{s,298} = \Delta H^0_s + \sum \Delta H^0_\sigma + \int_{298}^{T} \Delta C^0_p \, dT \qquad (18)$$

where $\Delta H^0_s = \Delta H^0_v + \Delta H^0_{fn}$; ΔH^0_s and ΔH^0_v represent the values for the enthalpy of sublimation and enthalpy of volatilization, respectively, as determined by us (Table 3); and ΔH^0_{fn} denotes the enthalpy of fusion. The

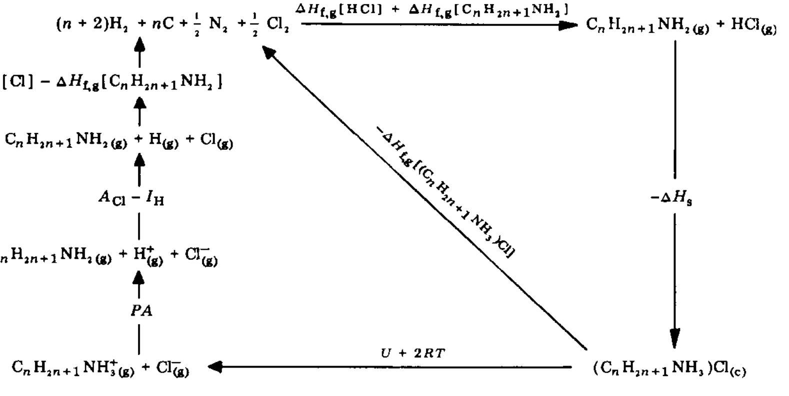

Fig. 1. The extended Born–Fajans–Haber cycle.

term $\Sigma\Delta H_\sigma^0$ arises from any polymorphic transitions which these salts may undergo between 298 K and the beginning of the fusion or sublimation process, and the term $\int_{298}^{T} \Delta C_p^0 \, dT$ accounts for the changes of enthalpy resulting from the heat capacities of the appropriate forms of $(C_nH_{2n+1}NH_3)Cl$. Equation (18) is adequate when the sublimation process is not preceded by melting. If melting occurs before the volatilization process $\Delta H_s^0 = \Delta H_v^0 + \Delta H_{fn}^0$.

Since pertinent data for ΔH_{fn}^0 of all the investigated amine hydrochlorides were not available [23,24,46], they were estimated by an empirical relationship related to the entropy of fusion (ΔS_{fn}^0) [65,66], i.e.

$$\Delta S_{fn}^0 = \frac{\Delta H_{fn}^0}{T_m} = \text{const.} \tag{19}$$

Using the experimental values available for ΔH_{fn}^0 [24,46] (for $n = 3$, 6, 7 and 8) and values of T_m derived in this work, the const. value was estimated to be equal to 13.6 J mole^{-1} K^{-1}. Assuming that the entropy of fusion is the same for any alkylammonium chloride, the values of ΔH_{fn}^0 could be estimated from eqn. (19) using the values of T_m derived in this work (Table 2). They are listed in Table 7. The values of $\Sigma\Delta H_\sigma^0$ were taken from the literature (Table 7).

The magnitude and sign of the heat capacity term is more difficult to assess in the absence of values for most of the salts and gaseous products. For the first compound of the series the heat capacity term is equal to ca. -7.0 kJ mole^{-1}. This value was evaluated within the temperature limits 298–500 K using available heat capacity data [66]. For other compounds of the series we assume the value of the heat capacity term to be the same as for NH_4Cl. Some idea of the validity of this assumption may be gauged from two facts. Firstly, volatilization of mono-*n*-alkylammonium chlorides proceeds in a temperature range similar to that for the sublimation of NH_4Cl. Secondly, the expected increase of the heat capacity caused by an increase of the size of the alkyl group should be identical for salts and appropriate amines. Thus, the change of the size of the alkyl group may not influence ΔC_p^0 values. Indeed, a similar regularity has been observed by Bergstrom and Olofsson [69] during a study of the dissociation of alkylammonium chlorides in aqueous solutions.

The derived values of $\Delta H_{s,298}^0$ for all the compounds investigated are listed in Table 8.

Enthalpy of formation of $(C_nH_{2n+1}NH_3)Cl$

From the thermodynamic cycle presented in Fig. 1, values of $\Delta H_{f,c}^0$ for $(C_nH_{2n+1}NH_3)Cl$ can be calculated from the equation

$$\Delta H_{f,c}^0[(C_nH_{2n+1}NH_3)Cl] = \Delta H_{f,g}^0[C_nH_{2n+1}NH_2] + \Delta H_{f,g}^0[HCl] - \Delta H_s^0 \tag{20}$$

TABLE 7

Ancillary data for the evaluation of thermochemical parameters

n	$(C_nH_{2n+1}NH_3)Cl$				$C_nH_{2n+1}NH_2$	
	ΔH^0_{fn} (kJ mole^{-1})		$\Sigma\,\Delta H^0_\sigma$ (kJ mole^{-1})		Molecular parachor [66] ($J^{1/4}m^{5/2}$)	ΔH^0_v [73] (kJ mole^{-1})
	From literature	Used in calculations	From literature	Used in calculations		
0			4.06 [67] 4.66 [68]	4.4	309.3	
1		6.9			551.2	24.3
2	9.79 [24]	5.2	7.4 [39]	7.4	776.2	25.6
3	5.90 [24]	5.9	4.15 [24]	4.2	1001.2	30.6
4		6.6			1226.2	35.6
5		6.8			1451.2	40.6
6	6.56 [46] 9.88 [23]	6.7			1676.2	45.5
7	6.61 [24] 6.94 [46] 9.54 [23]	6.5	1.87 [24]	1.9	1901.2	50.5
8	6.36 [24] 6.64 [46] 9.42 [23]	6.4	4.65 [24]	4.7	2126.2	55.5

Table 7 (continued)

n	$C_nH_{2n+1}NH_2$							
	At 298 K						PA (kJ mole^{-1})	
	$\Delta H^0_{f,l}$ [51][a] (kJ mole^{-1})	$\Delta H^0_{f,g}$ (kJ mole^{-1})						
		From literature	Evaluated			Used in calculations[b]	From literature [74]	Used in calculations[c]
			From eqn. (22)	From eqn. (21)	By the method described in ref. 66			
0		−45.9 [72] −46.2 [51]		12.1		−45.9	866.3	860.5
1	−47.1	−28.0 [51,66]	−22.8	−21.4	−28.0	−28.0	914.0	908.2
2	−73.5	−48.5 [51]	−47.9	−52.5	−51.8	−52.2	926.6	920.9
3	−100.8		−70.2	−83.7	−80.3	−82.0	932.4	925.9
4	−172.0		−136.4	−114.9	−108.8	−111.9	934.5	928.5
5				−146.0	−137.3	−141.7		929.9
6	−226.6		−181.1	−177.2	−166.1	−171.7		930.8
7	−250.1		−199.6	−208.4	−194.6	−201.5		931.4
8				−239.5	−223.1	−231.3		931.8

[a] Calculated from the standard enthalpy of combustion at 298 K.

[b] With the exception of the first two compounds of the series, these values present the mean from the two preceding columns

[c] Calculated using eqn. (28).

TABLE 8

Thermochemical parameters of mono-*n*-alkylammonium chlorides at 298 K

n	$(C_nH_{2n+1}NH_3)Cl$						$C_nH_{2n+1}NH_3^+$	
	ΔH_s° (kJ mole^{-1})	$\Delta H_{f,c}^\circ$ (kJ mole^{-1})			U° (kJ mole^{-1})		$\Delta H_{f,g}^\circ$ (kJ mole^{-1})	
		This work [a]		From literature	This work	From literature	This work	From literature
		A	B					
0	168.2	−306.4		−314.4[12,70] −315.5[51,66]	697.4	676.3[63] 692[12] 697.7[64] 704.1[70]	629.8	624[12] 630.2[51,70] 631.1[64]
1	157.3	−277.6	−279.2	−285.9[51] −298.3[12]	638.8	656[12]	600.0	604[12]
2	167.6	−312.1	−312.3		636.4		563.1	
3	171.5	−345.8	−345.5		635.3		528.3	
4	176.6	−380.8	−378.6		637.8		495.8	
5	179.4	−413.4	−411.7		639.2		464.6	
6	183.7	−447.7	−444.9		642.6		433.7	
7	180.6	−474.4	−478.0		638.9		403.3	
8	186.8	−510.4	−511.1		644.7		373.1	

[a] A, evaluated using eqn. (20); B, calculated from the equation: $\Delta H_{f,c}^\circ[(C_nH_{2n+1}NH_3)Cl] = C_1P + C_2$, where $C_1 = -0.147$(kJ mole^{-1} J$^{-1/4}$ m$^{-5/2}$) and $C_2 = -198.0$ (kJ mole^{-1}).

To evaluate these values we need to know the standard enthalpies of formation of the appropriate amines at 298 K. Unfortunately, such data are not available for all the compounds investigated. Thus, we applied the empirical relationship of Voelkel and Tomasik [71] for the evaluation of $\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2]$. These authors found that for higher members of the series of primary n-alkylamines ($n \geqslant 3$), the standard enthalpies of formation can be estimated from the equation

$$\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2] = C_1P + C_2 \qquad (21)$$

where P is the molecular parachor (Table 7) and C_1 and C_2 are constants. Equation (21) may be considered as an approximation formula, i.e. some values of $\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2]$ are necessary to estimate values of both constants. Using values of the standard enthalpy of combustion of several liquid primary n-alkylamines as reported in the literature [51] and values of $\Delta H^0_{\mathrm{f,g}}[\mathrm{CO}_2] = -393.5$ kJ mole^{-1} [72] and $\Delta H^0_{\mathrm{f,l}}[\mathrm{H_2O}] = -285.8$ kJ mole^{-1} [72], we calculated values of $\Delta H^0_{\mathrm{f,l}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2]$ (see Table 7). Taking these values and the values of the enthalpy of vaporization (ΔH^0_{v}) estimated by Ducros et al. [73] (Table 7), it was possible to evaluate $\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2]$ from the equation

$$\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2] = \Delta H^0_{\mathrm{f,l}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2] + \Delta H^0_{\mathrm{v}} \qquad (22)$$

These values are listed in Table 7. Starting from these values it was possible to evaluate both the constants in eqn. (21), by applying the standard least-squares procedure. The values obtained were $C_1 = -0.139$ kJ mole^{-1} J$^{-1/4}$ m$^{-5/2}$ and $C_2 = 55.0$ kJ mole^{-1}, with the correlation coefficient equal to 0.986.

The standard enthalpies of formation of primary n-alkylamines were also estimated using an approximate method as described in ref. 66 (Table 7).

Using values of $\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2]$ (Table 7) together with the values of ΔH^0_{s} evaluated in this work (Table 8) and taking $\Delta H^0_{\mathrm{f,g}}[\mathrm{HCl}] = -92.3$ kJ mole^{-1} [66,72], we derived values of the standard enthalpy of formation of crystalline mono-n-alkylammonium chlorides (see Table 8). Examining these data it is noticed that they exhibit linear dependence on the molecular parachor (correlation coefficient equal to 0.9996) if we omit the value of $\Delta H^0_{\mathrm{f,c}}$ for $\mathrm{NH_4Cl}$ (see Table 8).

Crystal lattice energy

From the thermochemical cycle presented in Fig. 1, the following independent relations may be derived.

$$\begin{aligned} U^0 + 2RT + PA - I_{\mathrm{H}} + A_{\mathrm{Cl}} - \Delta H^0_{\mathrm{f,g}}[\mathrm{H}] - \Delta H^0_{\mathrm{f,g}}[\mathrm{Cl}] \\ - \Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2] \\ + \Delta H^0_{\mathrm{f,g}}[\mathrm{HCl}] + \Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_2] - \Delta H^0_{\mathrm{s}} = 0 \end{aligned} \qquad (23)$$

Since [64]

$$\Delta H^0_{f,g}[H^+] = \Delta H^0_{f,g}[H] + I_H \tag{24}$$

and

$$\Delta H^0_{f,g}[Cl^-] = \Delta H^0_{f,g}[Cl] - A_{Cl} \tag{25}$$

eqn. (23) may be rearranged to the form

$$U^0 = -PA - 2RT + \Delta H^0_{f,g}[H^+] + \Delta H^0_{f,g}[Cl^-] - \Delta H^0_{f,g}[HCl] + \Delta H^0_s \tag{26}$$

PA represents the proton affinity of appropriate amines, i.e. the negative values of the enthalpy of reaction (27) [74].

$$C_nH_{2n+1}NH_{2(g)} + H^+_{(g)} \rightarrow C_nH_{2n+1}NH^+_{3(g)} \tag{27}$$

Values of PA are usually established relative to the PA value of some reference compound. For the first five amines of the series, the PA values have been estimated by Aue et al. [74]. In this work, we used values which were lower by 5.8 kJ mole^{-1}. This results from the difference between the value of PA for NH_3 given by Aue et al. [74] and that reported by Jenkins and Morris [70], the latter being calculated from the crystal lattice energies of several ammonium salts. According to the suggestion of Aue et al. [74] we found that the values of PA reported for primary n-alkylamines satisfy the equation

$$PA^{-1} = 933.4^{-1} + \left[6140(n + 1.34)^2\right]^{-1} \tag{28}$$

where n represents the number of carbon atoms in the amine molecule. Thus, eqn. (28) could be used for estimation of PA of higher amines. Values of PA used in this work are listed in Table 7.

The values of other thermochemical parameters used in the estimation of U^0 were: $\Delta H^0_{f,g}[H^+] = 1536.2$ kJ mole^{-1} [63,66,70], $\Delta H^0_{f,g}[HCl] = -92.3$ kJ mole^{-1} [51,66,72] and $\Delta H^0_{f,g}[Cl^-] = -233.8$ kJ mole^{-1} [70]. The $\Delta H^0_{f,g}[Cl^-]$ values taken from several sources differ notably, e.g. -233.6 [66], -233.8 [70], -246.0 [75], -246.4 [15] and -247.8 [63]. We chose a value used by Jenkins and Morris [70] in the recent estimation of the lattice energies of some metal chlorides.

The derived values of the lattice energy (Table 8) show an initial sharp decrease, from $n = 0$ to $n = 1$, to a minimum for n-propylammonium chloride, followed by a gradual increase. One may notice, however, that the differences in lattice energies for compounds with $1 \leqslant n \leqslant 8$ are not significant, but are within experimental and computational uncertainties. The foregoing facts appear to give some justification for the assumption that values of U^0 do not depend on the length of the aliphatic chain of primary n-alkylamines.

Enthalpy of formation of the $C_nH_{2n+1}NH_3^+$ *ions*

From eqn. (27) we obtain

$$\Delta H^0_{f,g}[C_nH_{2n+1}NH_3^+] = \Delta H^0_{f,g}[C_nH_{2n+1}NH_2] + \Delta H^0_{f,g}[H^+] - PA \qquad (29)$$

Using the appropriate ancillary data from Table 7 and values reported earlier in the text, we estimated values of the standard enthalpy of formation of the *n*-alkylammonium ions (see Table 8).

This work provides the important thermochemical characteristics for several primary *n*-alkylammonium chlorides, not previously available in the literature. Undoubtedly, the values derived are approximate because of the numerous assumptions and approximations introduced during the calculations. Moreover, the experimental method (dynamic thermogravimetry) which was applied is really a non-equilibrium technique. Thus, the values of ΔH_s^0 evaluated may be loaded by an error which is difficult to assess. Nevertheless, the agreement between the values of the thermochemical parameters derived by us and those available in the literature is quite good.

The data from this work show clearly that values of basic thermochemical parameters depend on the length of the chain in the amine molecule. However, to establish the general trends in the changes of thermochemical properties with structure of the alkyl substituent, it would seem to be adequate to extend investigations to more complex aliphatic amines.

ACKNOWLEDGEMENTS

The author would like to thank Prof. J. Szychlinski for valuable discussion and Mrs. E. Kowalewska and Mrs. I. Nikel for experimental assistance.

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APPENDIX A

In eqn. (17), α and T represent variables, whereas E, X_1 and X_2 are parameters which are characteristic of the process. The sum of the squares error is given by [61]

$$\mathrm{F}(E, X_1, X_2) = \sum_{i=1}^{N} \left(X_2 A_i + \tfrac{1}{2} B_i - \frac{X_1}{3\Phi} C_i \right)^2 \tag{A1}$$

where the subscript i designates the ith data point and N is the number of data points taken. In eqn. (A1) A_i, B_i and C_i denote, respectively

$$A_i = T_i \left[1 - (1 - \alpha_i)^{1/3} \right]$$

$$B_i = 1 - (1 - \alpha_i)^{2/3}$$

$$C_i = T_i^{3/2} \mathrm{e}^{-E/2RT_i}$$

The best set of parameters should meet the conditions

$$\frac{\partial \mathrm{F}(E, X_1, X_2)}{\partial E} = \frac{X_1}{3R\Phi} \sum \frac{C_i}{T_i} \left(X_2 A_i + \tfrac{1}{2} B_i - \frac{X_1}{3\Phi} C_i \right) = 0 \tag{A2}$$

$$\frac{\partial \mathrm{F}(E, X_1, X_2)}{\partial X_1} = -\frac{2}{3\Phi} \sum C_i \left(X_2 A_i + \tfrac{1}{2} B_i - \frac{X_1}{3\Phi} C_i \right) = 0 \tag{A3}$$

$$\frac{\partial \mathrm{F}(E, X_1, X_2)}{\partial X_2} = 2 \sum A_i \left(X_2 A_i + \tfrac{1}{2} B_i - \frac{X_1}{3\Phi} C_i \right) = 0 \tag{A4}$$

All the summations are taken from 1 to N. Unfortunately, eqns. (A2)–(A4) are non-linear towards E and it is difficult to solve them simultaneously. A rather cumbersome approach allowing one to resolve such a problem has been given by Chen and Fong [62]. We applied a simpler procedure which leads to the system of linear equations. Under a profile of E = constant, it is possible to calculate values of C_i and thus also X_1 and X_2 from the equations

$$X_1 = 3\Phi X_2 \frac{\sum A_i C_i}{\sum C_i^2} + \frac{3\Phi}{2} \frac{\sum B_i C_i}{\sum C_i^2} \tag{A5}$$

$$X_2 = \frac{\frac{1}{2}\left[\left(\sum A_i C_i \times \sum B_i C_i / \sum C_i^2\right) - \sum A_i B_i\right]}{\sum A_i^2 - \left(\sum A_i C_i\right)^2 / \sum C_i^2} \tag{A6}$$

The use of values of X_1 and X_2 evaluated at an assumed value of E allows calculation of values of Y_i based on eqn. (A7).

$$X_2 A_i + \frac{1}{2} B_i - \frac{X_1}{3\Phi} C_i = Y_i \tag{A7}$$

Further, we assume that the best fit of eqn. (17) to the experimental data is attained when the δ function, given by eqn. (A8), reaches a minimum.

$$\delta = \frac{\sqrt{\sum Y_i^2}}{N} \tag{A8}$$

To find the minimum of the δ function, we applied a trial-and-error procedure. Variation in E is not, however, completely free. We restricted our investigations to values of E which were close to the appropriate values of the enthalpy of evaporation.