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THERMAL PROPERTIES OF H_2SnCl_6 COMPLEXES. PART II. THERMAL FEATURES OF ALKANAMINIUM HEXACHLOROSTANNATES

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ABSTRACT

Thermoanalytical methods (DTA, TG and DTG) were used to investigate the thermal behaviour of unbranched complex salts with the general formula $[(C_nH_{2n+1})_pNH_{4-p}]_2SnCl_6$ (where $n = 1-4$ and $p = 2–4$) and several other cyclic and open chain branched aliphatic alkanaminium hexachlorostannates. The thermal dissociation of these compounds can generally be summarized using the equation

$$(A_pNH_{4-p})_2SnCl_6(c) \rightarrow SnCl_4(g) + 2aHCl(g) + 2A_{p-s}NH_{3-p+s}(g) + 2(1-a)ACl(g)$$

where A denotes alkyl group ($a = 0$ and $s = 1$ for quaternary and $a = 1$ and $s = 0$ for other compounds studied). The thermolysis of derivatives with a simple structure occurs in one step and leads to their total volatilization. The decomposition of other compounds, usually with a complex structure, is accompanied by side reactions.

The experimental TG curves were used to examine the thermodynamics and kinetics of thermolysis. The enthalpies of the thermal dissociation were evaluated on the basis of the van't Hoff equation. The derived values, together with the available literature data, were used to determine the enthalpy of formation and the crystal lattice energy of the salts. The latter quantity was also examined using the Kapustinskii–Yatsimirskii formula. The kinetics of volatilization were analysed using the Jacobs and Russell-Jones theory for the dissociative volatilization process and a standard approach based on the Arrhenius model.

The values of the parameters characterizing the thermal properties of alkanaminium hexachlorostannates, i.e. temperatures of the thermal effects, and the thermochemical and kinetic constants of thermolysis, depend on the number, length and structure of the alkyl substituent. The essential thermal and thermochemical characteristics of the compounds are thoroughly reviewed and discussed.

INTRODUCTION

The elements of group IV (M) form two series of chlorides, i.e. dichlorides (MCl_2) and tetrachlorides (MCl_4). The stability of the dichlorides increases with an increase in the mass of M. The stability of the MCl_4 compounds exhibits a reverse tendency [1]. Thus the most stable dichloride is $PbCl_2$, whereas CCl_2 is thermodynamically unstable. On reviewing the enthalpies of formation of MCl_4 (ref. 1, Table 1) it can be seen that all the compounds

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are thermodynamically stable; however, the values of $\Delta H^{\ominus}_{f,298}$ decrease with an increase in M. Only CCl_4 does not follow this tendency. The decomposition of the tetrachlorides to the corresponding dichlorides and a chlorine molecule requires that a significant thermochemical barrier is overcome (an exception is $PbCl_4$, where the process is exothermic [1]). This feature of $PbCl_4$ results from the relatively high Pb^{4+}/Pb^{2+} redox potential (+1.5 V [2]) compared with that of $Cl_2/2\ Cl^-$ (+1.36 V [3]). $SnCl_4$, which shows many similarities to $PbCl_4$, does not decompose spontaneously to $SnCl_2$(c) and Cl_2(g) since the Sn^{4+}/Sn^{2+} redox potential is only +0.15 V [2]. All MCl_4 derivatives exhibit distinct electroacceptor properties which become more pronounced with an increase in M. The tetrachlorides of Ge, Sn and Pb form octahedral MCl_6^{2-} ions [4–10] which are much more stable than their precursors [1].

To shed more light on the chemistry of the tetrachlorides of the group IV elements it is important to reveal the general features regarding the behaviour of tin and lead chlorides. Our earlier research was devoted to the thermochemistry of $PbCl_4$ derivatives [11]. In the first paper of this research we reported the results of thermoanalytical investigations on primary *n*-alkanaminium hexachlorostannates [1]. This work is a continuation of that research and its primary objectives are to elucidate the general features governing the thermal decomposition of alkanaminium hexachlorostannates and to establish correlations between the structure of the amine and the thermochemistry and thermal properties of these complex salts. This study also provides information on the behaviour of highly unsymmetrical ions. Moreover, information on the kinetics of the dissociative sublimation process is presented.

EXPERIMENTAL

All amines of pure or analytical grade were used as received. Other reagents were of analytical grade. Alkanaminium hexachlorostannates were synthesized using methods described in the literature [6,12]. Thus the aqueous solutions of alkanaminium chlorides were added stoichiometrically to dilute HCl solutions of $SnCl_4 \cdot 5\ H_2O$ (molar ratio, 2:1). The crystals formed were filtered, washed with 0.1 M HCl solution, and dried in a vacuum desiccator over NaOH and P_2O_5. The quaternary salts pyrrolidinium and cyclohexanaminium hexachlorostannates were additionally recrystallized from acetonitrile or mixtures of acetonitrile and ethyl ether. The compositions of the compounds were confirmed by elemental analysis.

The thermal analyses were carried out using an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference in a dynamic atmosphere of N_2. The samples weighing 100 mg were placed on one platinum plate of the polyplate sample holder (ref. 13, Appendix 1, No. 4). Other operating conditions were

TABLE 1

α vs. T for the thermal dissociation of $[(CH_3)_2CHNH_3]_2SnCl_6$ (A) and $\{[(CH_3)_2CHCH_2]_2NH_2\}_2SnCl_6$ (B) (see Fig. 1)

	α									
	0.08	0.16	0.24	0.32	0.40	0.48	0.56	0.64	0.72	0.80
A, T (K)	512.0	527.7	537.7	546.0	552.0	556.3	560.7	565.3	569.0	574.7
B, T (K)	492.8	507.8	517.2	523.5	529.0	534.3	538.2	542.5		

as follows: heating rate, ca. 5 K min^{-1}; sensitivities of DTG, DTA and TG galvanometers, $\frac{1}{10}$, $\frac{1}{3}$ or $\frac{1}{2}$ and 100 mg, respectively. All compounds examined were ground in an agate mortar before analysis. Some were heated in vacuo (in a vacuum pistol) prior to analysis at temperatures below the onset of volatilization.

In the case of the primary, secondary and tertiary alkanaminium hexachlorostannates the thermogravimetric curves were used to examine the thermodynamics and kinetics of the decomposition process. From the TG curves (such as those shown in Fig. 1) the temperatures T corresponding to certain degrees of volatilization α were determined as described previously [14]. The range of α over which these data points were established was chosen by examination of the pattern of all the thermoanalytical curves; it extended over the range where no side reactions occurred. Each α vs. T data point was determined from at least three replicate measurements. An example is given in Table 1.

RESULTS AND DISCUSSION

General features of the thermal decomposition

The thermoanalytical curves obtained for two compounds (chosen as examples) are shown in Fig. 1. The essential parameters characterizing the thermal dissociation of all the compounds studied, determined on the basis of thermoanalytical investigations, are compiled in Table 2. Numerous similarities can be seen. The thermal decomposition of several hexachlorostannates of monoalkyl and dialkyl substituted amines, i.e. compounds 1, 2, 7, 10, 15, 17 and 19, is accompanied by the total volatilization of the solid substrate (Fig. 1(A)). Two distinct stages are always observed in the TG curves of these derivatives. The first rapid step, in which up to 70% of the sample volatilizes, is followed by a slow step (seen as a "tail"), in which the remaining part of the sample disappears. A similar phenomenon has also been observed during the thermal dissociation of several other compounds [1,16,18–20]. The explanation of this effect requires kinetic considerations

TABLE 2

Thermal characteristics of alkanaminium hexachlorostannates

Compound [a]		Peak temperature [b] (K)							Temperature [b] (K)			Parameters of the onset of the second stage	
No.	Formula	DTG	DTA						$T_{0.08}$	$T_{0.72}$	ΔT_α		
			T_σ		T_m [c]		T_p						
			This work	From literature	This work	From literature	Endo	Exo				α	T (K)
1	$[(CH_3)_2NH_2]_2SnCl_6$	581			578	562 [15]	583		524.0	583.2	59.2	0.79	590
					(575–579; D)								
2	$[(CH_3)_3NH]_2SnCl_6$	574	499		555	573; D [15]	574		517.3	583.3	66.0	0.74	587
			538		(555–563; D)								
3	$[(CH_3)_4N]_2SnCl_6$	652					623						
							656	682					
4	$[(C_2H_5)_2NH_2]_2SnCl_6$	570	419		544	533; D [15]	551		521.5				
		652			(545–549; D)		568	663					
5	$[(C_2H_5)_3NH]_2SnCl_6$	567	387		521	541; D [15]	555		519.3				
		657			(519–523; D)			679					
6	$[(C_2H_5)_4N]_2SnCl_6$	592		323 [15]	592			616					
		624			(593; D)			639					
								677					
7	$[(n\text{-}C_3H_7)_2NH_2]_2SnCl_6$	555	337		422		545		502.3			0.68	565
		625	415		(416)		596	629					
8	$[(n\text{-}C_3H_7)_3NH]_2SnCl_6$	547	410		489		590		492.8				
		630			(479–485; D)			637					
9	$[(n\text{-}C_3H_7)_4N]_2SnCl_6$	562			436			562					
		571			(448–452; D)		573						
		651						648					
10	$[(CH_3)_2CHNH_3]_2SnCl_6$	566			571		568		512.0	569.0	57.0	0.80	574

					(573–575; D)							
11	$\{[(CH_3)_2CH]_2NH_2\}_2SnCl_6$	563			469	552		508.5				
		644			(447–453)		649					
12	$[(n\text{-}C_4H_9)_2NH_2]_2SnCl_6$	557	413		433	547		507.0				
					(410–420)							
13	$[(n\text{-}C_4H_9)_3NH]_2SnCl_6$	545	393		407		553	485.3				
					(381–385)		636					
							722					
14	$[(n\text{-}C_4H_9)_4N]_2SnCl_6$	526	344		(523–526; D)	528						
		575	373				570					
		609	407				632					
15	$[(CH_3)_2CHCH_2NH_3]_2SnCl_6$	558				561		498.0	564.0	66.0	0.79	577
16	$[(CH_3)(C_2H_5)CHNH_3]_2SnCl_6$	554	437		519	545		505.3	564.3	59.0		
					(516–520; D)							
17	$[(CH_3)_3NH_3]_2SnCl_6$	554			504	554		495.3	558.3	63.0	0.81	565
18	$\{[(CH_3)_2CHCH_2]_2NH_2\}_2SnCl_6$	541			484	535		492.8				
					(483–488; D)							
19	$[(CH_3)_2CH(CH_2)_2NH_3]_2SnCl_6$	575	361	363 [15]	513	575		522.3	578.0	55.7	0.79	582
20	$(c\text{-}C_6H_{11}NH_3)_2SnCl_6$	565	368		511	549		514.0				
		615	493		(533–537; D)	613						
21	$(C_4H_8NH_2)_2SnCl_6$	574			503	571		539.0				
		648			(496–500)		691					
22	$(C_5H_{10}NH_2)_2SnCl_6$	583			544	580		529.7				
		654			(541–544; D)							
		688					694					

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[a] For names of amines see ref. 16, Table 2. [b] The symbols were taken from ref. 17. T_p = temperature of the peak, T_σ = temperature of the solid state phase transition, T_m = temperature of melting, T_α = temperature at which the extent of conversion is equal to α (i.e. $T_{0.08} = T_{\alpha=0.08}$) and $\Delta T_\alpha = T_{0.72} - T_{0.08}$. [c] The melting temperature determined using the standard capillary method is given in parentheses; D indicates melting with decomposition.

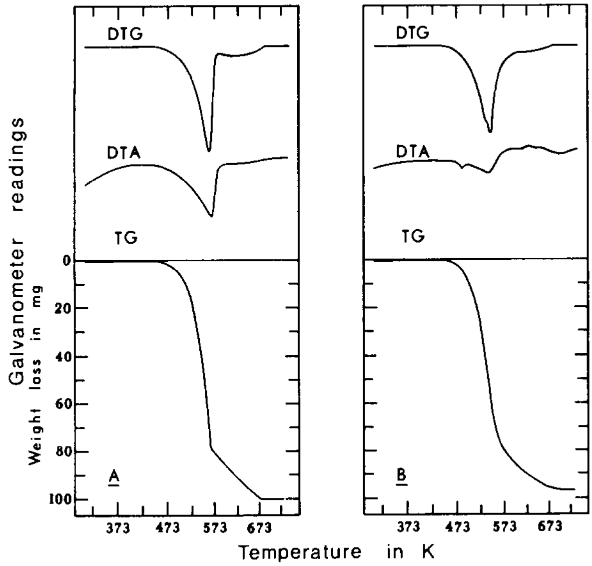

Fig. 1. Thermal analyses of 2-propanaminium hexachlorostannate (A) and 2-methyl-*N*-(2-methylpropyl)-1-propanaminium hexachlorostannate (B).

which will be presented later. The thermolysis of several other compounds, i.e. 4, 5, 8, 11, 12, 13, 16, 18, 20, 21 and 22, proceeds in a similar manner to that of the above-mentioned derivatives at the beginning of volatilization; however, at the end of the process side reactions occur. The thermoanalytical curves (Fig. 1(B)) obtained in these cases are not typical. Moreover, a solid residue is left in the sample holder. Quaternary salts demonstrate a rather complex thermal decomposition pattern. The compounds undergo partial volatilization on heating accompanied by the formation of a residue.

The nature of the gaseous and solid products was not examined in this study. By analogy with the thermolysis of other similar systems [1,16,18–20], it may be expected that the gaseous phase formed during the dissociation of the hexachlorostannates which exhibit a simple decomposition pattern is composed of $SnCl_4$, HCl and the appropriate amine. The appearance of solid products undoubtedly results from the participation of side processes. The solid residues (white or white-grey in colour) are presumably composed of SnO_2 which may be contaminated with the carbonization products of the organic fragments of the molecules. The formation of SnO_2 under the experimental conditions used in this study can be explained by the fact that oxygen is always present in small amounts in the reaction zone due to the leaks in the oven of the derivatograph [21].

The thermal dissociation of some of the compounds is preceded by solid phase transitions or melting (Table 2). The comparison of literature melting point values and those determined using the standard capillary method with some peak temperatures in the DTA curves permitted the identification of the thermal effects resulting from fusion. The thermal effects which occurred before melting were identified as solid phase transitions. From the data in Table 2 it can be seen that no similarities can be observed in the appearance of the phase transitions or melting.

The characteristic temperatures of the thermal decomposition, i.e. T_p (from DTA and DTG curves), $T_{0.08}$, $T_{0.72}$ and ΔT_α, show a slight dependence on the length and structure of the alkyl substituents in the amine. The T_p values usually decrease with an increase in the size of the alkanaminium cation. It is also worth noting that the temperatures of the onset of decomposition of alkanaminium hexachlorostannates [1] are markedly higher than those characteristic of the corresponding chloride salts [16,20].

Nature of the thermal process

The mechanism of the dissociative volatilization of hexachlorostannates of primary alkanamines was analysed in detail in the first paper of this series [1]. The primary decomposition step involves the release of $SnCl_4$, HCl and the amine molecules as a gaseous phase. The thermal dissociation of hexachlorostannates of secondary and tertiary alkanamines should proceed in a similar manner. A difference may be expected for quaternary salts. By analogy with the thermal decomposition of the corresponding chlorides [16] it may be assumed that the primary step in the thermolysis of quaternary alkanaminium hexachlorostannates involves the volatilization of $SnCl_4$ accompanied by a destruction of the remaining fragments of the molecules to the corresponding tertiary amines and chloroalkanes. Neglecting the possible weak interactions of the decomposition fragments in the gaseous phase [1], the primary thermal decomposition of the hexachlorostannates of alkanamines can thus be summarized as follows

$$\begin{aligned}(A_pNH_{4-p})_2SnCl_6(c) \rightarrow SnCl_4(g) + 2aHCl(g) + 2A_{p-s}NH_{3-p+s}(g) \\ + 2(1-a)ACl(g) \qquad (1)\end{aligned}$$

where A denotes an alkyl group ($a = 0$ and $s = 1$ for quaternary and $a = 1$ and $s = 0$ for other compounds studied).

A thorough analysis of the thermoanalytical data reveals that the decomposition of some of the alkanaminium hexachlorostannates is well approximated by eqn. (1). Unfortunately, the simple course of the decomposition is complicated by secondary side reactions. Since the dissociation of the alkanaminium hexachlorostannates is initiated at relatively high temperatures, the destruction of the organic fragments of molecules can occur, and this is particularly pronounced during the thermolysis of salts containing cations of complex structure. Moreover, the $SnCl_4$ evolved may react with traces of oxygen or water, which are present in the reaction zone, to form SnO_2. These two processes do not explain all the pathways for side reac-

TABLE 3

Thermodynamic and kinetic constants for the volatilization of alkanaminium hexachlorostannates

Compound (Table 2)	Thermodynamic constants		Kinetic constants					Range of α [d]
	From eqn. (2) [a]		From the Jacobs and Russell–Jones model: eqn. (4) [b]			From the contracting surface area equation [c]		
	$\Delta H_v^\ominus$ (kJ mol^{-1})	Constant	E (kJ mol^{-1})	X_1 (K$^{-1/2}$ s^{-1})	X_2 (K^{-1})	$E^\star$ (kJ mol^{-1})	Z (s^{-1})	
1	474	19.2	450	470	-3.7×10^{-4}	100	7.0×10^{4}	0.08–0.72
2	417	16.9	371	16	-4.6×10^{-4}	87.8	5.2×10^{3}	0.08–0.72
4	417	16.8	210	0.0045	-1.3×10^{-3}	85.5	2.6×10^{3}	0.08–0.56
5	369	14.6	150	0.00026	-1.3×10^{-3}	74.2	2.1×10^{2}	0.08–0.48
7	412	17.3	223	0.016	-1.2×10^{-3}	85.8	5.9×10^{3}	0.08–0.64
8	342	14.2	172	0.0013	-1.3×10^{-3}	68.8	1.5×10^{2}	0.08–0.48
10	458	19.1	371	18	-7.1×10^{-4}	98.5	7.9×10^{4}	0.08–0.80
11	386	15.7	303	0.65	-8.6×10^{-4}	79.0	9.1×10^{2}	0.08–0.56
12	416	17.3	280	0.21	-1.1×10^{-3}	85.3	4.6×10^{3}	0.08–0.56
13	337	14.2	275	0.38	-8.4×10^{-3}	68.6	1.9×10^{2}	0.08–0.56
15	397	16.6	351	8.0	-8.1×10^{-4}	83.8	3.9×10^{4}	0.08–0.72
16	452	19.1	254	0.075	-1.1×10^{-3}	95.5	5.6×10^{4}	0.08–0.72
17	409	17.3	288	0.48	-9.4×10^{-4}	87.6	1.1×10^{4}	0.08–0.80
18	469	20.4	444	1500	-3.3×10^{-4}	98.3	1.9×10^{5}	0.08–0.64
19	499	20.5	488	3900	8.2×10^{-5}	106	2.8×10^{5}	0.08–0.72
20	408	16.6	227	0.011	-1.3×10^{-3}	82.6	1.9×10^{3}	0.08–0.64
21	447	17.5	258	0.027	-1.2×10^{-3}	89.2	3.1×10^{3}	0.08–0.32
22	381	14.8	193	0.00079	-1.4×10^{-3}	75.3	1.9×10^{2}	0.08–0.32

[a] Values of $\Delta H_v^\ominus$ and constant were determined by applying a standard least-squares procedure. The linear correlation coefficient was always better than 0.995. [b] Values of X_1, X_2 and E were derived using a least-squares procedure described in ref. 20 with a modification introduced in ref. 1. [c] $1-(1-\alpha)^{1/2} = Z(T/\Phi)\exp[-E^\star/(RT)]$. [d] The thermal dissociation range over which α vs. T data points were drawn from the TG curves.

tions. Rather they indicate a possible explanation for the observed complex course of thermolysis for some of the compounds studied. The nature of these side processes is not very interesting from the thermochemical point of view and, therefore, we did not devote much attention to its detailed examination.

Thermodynamics of the thermal dissociation

The enthalpy of volatilization $\Delta H_v^\ominus$ was determined on the basis of the van't Hoff equation using experimental α vs. T dependences. The volatilization of 1 mole of alkanaminium hexachlorostannate results in the formation of 5 moles of gaseous products. Hence, based on our previous considerations [1,14,16], $\Delta H_v^\ominus$ values can be evaluated from the equation

$$\ln \alpha = -\frac{\Delta H_v^\ominus}{5R}\frac{1}{T} + \text{constant} \qquad (2)$$

where R is the gas constant. The enthalpies of volatilization thus derived are listed in Table 3.

Kinetics of thermolysis

From the physical point of view the dissociative volatilization presents a fairly simple process. Nevertheless, as yet no coherent theory has been proposed to account for the kinetics of this phenomenon. The most adequate theory available to explain the kinetics seems to be the phenomenological surface diffusion model outlined originally by Jacobs and Russell-Jones [22]. In several earlier studies we have demonstrated that this approach adequately explains the kinetics of volatilization of alkanaminium chlorides [16,20], hydrochlorides of aromatic amines [19] and aromatic bases [18], and hexachlorostannates of primary *n*-alkanamines [1]. A detailed discussion regarding this theory, as well as its adaptation to non-isothermal conditions, has been given elsewhere [20]. The final form of the integral equation which describes the kinetics of volatilization of primary, secondary and tertiary alkanaminium hexachlorostannates at linearly increasing temperature [1] is

$$\left(X_2 T - \frac{\Delta}{a_0}\right)\left[1-(1-\alpha)^{1/3}\right] + \tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]$$
$$-\left(\frac{\Delta}{a_0}\right)^2 \ln\left[\frac{(1-\alpha)^{1/3}+\Delta/a_0}{1+\Delta/a_0}\right] = \tfrac{1}{3}\frac{X_1}{\Phi}T^{3/2}\exp[-E/(5RT)] \qquad (3)$$

X_1, X_2 and E are constants and E can be identified with the kinetic energy barrier for the process. Φ is the heating rate, a_0 is the initial radius of particles from which the sublimation process occurs and Δ is the distance between collisions (i.e. the distance which a molecule travels, after leaving the condensed phase, before a collision occurs). At moderate pressures of a foreign gas (P = atmospheric pressure) $\Delta \ll a_0$ and the influence of the Δ/a_0 term on the kinetics of sublimation is relatively small. This takes place at the beginning of the process and then eqn. (3) can be reduced to the form

$$X_2T\left[1-(1-\alpha)^{1/3}\right]+\tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]=\tfrac{1}{3}\frac{X_1}{\Phi}T^{3/2}\exp[-E/(5RT)] \qquad (4)$$

However, the dissociative volatilization process may be considered to be a solid phase reaction. Therefore, the kinetics of this process can be approximated using the general equation [23]

$$g(1-\alpha)=Z\frac{T}{\Phi}\exp[-E^\star/(RT)] \qquad (5)$$

which is derived from the Arrhenius equation. In eqn. (5), $g(1-\alpha)$ represents the kinetic model for the process and Z and $E^\star$ are the Arrhenius constants ($E^\star$ identifies the activation barrier for the process).

Using the experimental α vs. T dependences and eqn. (4) the values of X_1, X_2 and E were evaluated by the method described elsewhere [1,20]. To derive the values of Z and $E^\star$, eqn. (5) was fitted to the experimental data points using a standard least-squares procedure. Fourteen different $g(1-\alpha)$ functions, describing the most common physical models for solid state reactions, were considered in these calculations [14]. As an example the values of the kinetic constants for the surface contracting area model (R2) are listed in Table 3.

The application of the Jacobs and Russell-Jones equation enabled us to fit the experimental data points quite well. Values of E (the activation barrier for the process) vary randomly. Moreover, they do not show any correlation with the structure and size of the alkanaminium cation. To study the problem in more detail, we estimated values of $E/\Delta H_v^\ominus$. If the volatilization of the primary, secondary and tertiary alkanaminium hexachlorostannates proceeds according to one distinct mechanism roughly the same values of this ratio might be expected. Indeed, our earlier studies on the thermolysis of alkanaminium chlorides [16,20], hydrochlorides of aromatic amines [19] and nitrogen aromatic bases [18] revealed such a relationship. In the first paper of this series [1] the values of E were only slightly lower than $\Delta H_v^\ominus$. It seems, therefore, that the values of E, X_1 and X_2 derived in this work exhibit features of purely mathematical constants without any true physical significance. It is rather difficult to account for the fact that the values of E are so scattered. A possible explanation may be that this results from the optimization procedure applied. Owing to the behaviour of the statistical method, the minimum of a function indicating the goodness of a fit is very flat and even minor changes in experimental values of T bring about major changes in the values of the constants. This effect becomes more pronounced if the number of experimental pairs of points decreases. Therefore, experimental uncertainties significantly influence the derived values of the constants.

Despite the fact that the Jacobs and Russell-Jones equation does not provide quantitative information on the kinetics of volatilization of the compounds, this model qualitatively accounts for the existence of a slow stage in the volatilization process of some of the compounds (1, 2, 7, 10, 15, 17 and 19; Table 2) as seen on the TG curves (see, for example, Fig. 1(A)). As has been pointed out earlier the term Δ/a_0 in eqn. (3) is negligibly small for a large part of the volatilization and can be neglected. However, at the end of the process the mean free path of the molecules Δ increases in comparison with the initial dimensions of the drops or crystals, and Δ approaches a_0 in magnitude. This causes a gradual decrease in the rate of volatilization since both terms involving Δ/a_0 in eqn. (3) are negative. This effect is of a general nature and has been observed during the non-isothermal volatilization of a number of other derivatives [1,16,18–20].

The physical models proposed so far for the description of the mechanism of the dissociative volatilization of alkanaminium salts indicate that the process is rather simple and proceeds in just a few steps [22,24]. If only one step determines the kinetics of such a process the simple Arrhenius model can be applied [23]. Following this approach, however, the activation energy derived should be at least equal to $\Delta H_v^\ominus$. This results from the fact that the process is exothermic (Table 3) and the molecule in an activated state has to reach at least the energy level resulting from the thermodynamic requirements. The examination of the kinetics of the thermal decomposition of hexachlorostannates using eqn. (5) reveals that the values of $E^\star/\Delta H_v^\ominus$ are almost constant for various compounds. Furthermore, the values of this ratio are characteristic of a given reaction model, and this is demonstrated in Table 4. However, none of the values of $E^\star$ approaches $\Delta H_v^\ominus$ in magnitude. On the basis of a general knowledge of solid state reactions and taking into account the conditions of the experiment, it is very probable that the process occurs on the surface of the condensed phase and thus is governed by the R2 mechanism. By using the appropriate $g(1-\alpha)$ function we obtained a very good approximation of the experimental curves. However, for the R2 mechanism the values of $E^\star$ are exactly five times lower than the corresponding $\Delta H_v^\ominus$ values. The question thus remains of how to account for such low values of the apparent activation energy. When considering this problem in our previous studies [1,16] we pointed out that apparent difficulties in the interpretation of $E^\star$ may be concealed in eqn. (5). For the dissociative volatilization process it may, perhaps, be more adequate to consider the Arrhenius equation against the number of gaseous products released from the simplest structural unit of the molecule. Such an approach implies that the transition state for the dissociative volatilization of hexachlorostannates of amines is a loosely bound complex of two molecules

TABLE 4

The ratio of $E^{\star}/\Delta H_{\mathrm{v}}$ for various reaction models

	Mechanism of the process[a]													
	R1	R2	R3	P1	P2	P3	P4	F1	A2	A3	D1	D2	D3	D4
$E^{\star}/\Delta H_{\mathrm{v}}^{\ominus}$	0.19	0.20	0.21	0.14	0.12	0.089	0.039	0.23	0.11	0.069	0.39	0.41	0.44	0.42

[a] For details see ref. 14, Table 1.

of HCl, two molecules of amine and an $SnCl_4$ molecule. Then, following the suggestion of Meshi and Searcy [25], the exponent in the kinetic equation is of the form $\exp[-E^{\star}/(5RT)]$, and all the values of $E^{\star}$ are a factor of 5 higher compared with those derived from eqn. (5). The application of eqn. (5), with the above modification, to the contracting surface area model leads to values of $E^{\star}$ which are exactly equal to the corresponding $\Delta H_{v}^{\ominus}$ values. This means that the dissociative volatilization process does not have to overcome any kinetic barrier other than that resulting from the thermodynamic requirements. The coincidence of the modified values of $E^{\star}$ and $\Delta H_{v}^{\ominus}$ may, of course, be fortuitous; nevertheless it strongly supports the idea that the process is realized close to the equilibrium state. The latter concept forms the framework on which all thermochemical considerations are based.

Thermochemical characteristics

The main aim of thermoanalytical investigations is to obtain some information on the thermochemistry of the systems examined. In our earlier studies we have shown that a knowledge of the enthalpy of volatilization of alkanaminium chlorides [16,20] and hydrochlorides of aromatic bases [18] and amines [19] enables an evaluation to be made of two important quantities, i.e. the enthalpies of formation and the crystal lattice energies. In ref. 1 we demonstrated that similar characteristics for alkanaminium hexachlorostannates can also be evaluated from a simple thermochemical cycle. The relationships derived in ref. 1 are generally valid for other alkanaminium hexachlorostannates, and therefore we used them in this work.

$$\begin{aligned}
&\Delta H_{f,c}^{\ominus}\left[(A_pNH_{4-p})_2SnCl_6\right]\\
&\quad = 2\Delta H_{f,g}^{\ominus}\left[A_{p-s}NH_{3-p-s}\right] + 2a\Delta H_{f,g}^{\ominus}[HCl] + 2(1-a)\Delta H_{f,g}^{\ominus}[ACl]\\
&\qquad + \Delta H_{f,g}^{\ominus}[SnCl_4] - \Delta H_{v}^{\ominus} \qquad (6)
\end{aligned}$$

$$\begin{aligned}
U^{\ominus}\left[(A_pNH_{4-p})_2SnCl_6\right] &= 2\Delta H_{f,g}^{\ominus}\left[A_{p-s}NH_{4-p-s}^{+}\right] + \Delta H_{f,g}^{\ominus}\left[SnCl_6^{2-}\right]\\
&\quad - \Delta H_{f,c}^{\ominus}\left[(A_pNH_{4-p})_2SnCl_6\right] - 3RT \qquad (7)
\end{aligned}$$

All magnitudes in eqns. (6) and (7) refer to 298 K and 1 atm. pressure. $\Delta H_{f}^{\ominus}$ is the enthalpy of formation of a given species, $U^{\ominus} + 3RT$ is the lattice enthalpy, $U^{\ominus}$ is the lattice energy and $\Delta H_{v}^{\ominus}$ is the enthalpy of volatilization.

The values of the enthalpy of volatilization derived from eqn. (2) do not refer to 298 K and therefore they were modified according to the equation

$$\Delta H_{v,298}^{\ominus} = \Delta H_{v}^{\ominus} + \Delta H_{fn}^{\ominus} + \sum \Delta H_{\sigma}^{\ominus} - \int_{298}^{T} \Delta C_{p}^{\ominus}\, dT \qquad (8)$$

TABLE 5

Thermochemical quantities (in kJ mol^{-1}) for alkanaminium hexachlorostannates at 298 K [a]

Compound		Ancillary data			Thermochemical characteristics			
No.	Formula	$\Delta H_{fn}^\ominus$	$\Sigma \Delta H_\sigma^\ominus$	$\int_{298}^{T_{0.08}} \Delta C_p^\ominus \, dT$	$\Delta H_v^\ominus$	$\Delta H_{f,c}^\ominus$ [b]	$U^\ominus$	
							A [c]	B [d]
1	$(Me_2NH_2)_2SnCl_6$			10	484	−1178	1183	1275
2	$(Me_3NH)_2SnCl_6$		4	10	431	−1135	1098	1236
3	$(Me_4N)_2SnCl_6$				(434)	(−1117) −1113	(1034)	1208
4	$(Et_2NH_2)_2SnCl_6$		2	10	429	−1231	1090	1257
5	$(Et_3NH)_2SnCl_6$		2	10	381	−1223	990	1238
6	$(Et_4N)_2SnCl_6$				(349)	(−1231) −1213	(880)	1206
7	$(n\text{-}Pr_2NH_2)_2SnCl_6$	5.7	4	10	432	−1321	1076	1248
8	$(n\text{-}Pr_3NH)_2SnCl_6$	6.7	2	10	361	−1340	951	1208
9	$(n\text{-}Pr_4N)_2SnCl_6$				(316)	(−1375) −1375	(834)	1165
10	$(i\text{-}PrNH_3)_2SnCl_6$			10	468	−1292	1175	1298
11	$(i\text{-}Pr_2NH_2)_2SnCl_6$	6.4		10	402	−1347	1030	1257
12	$(n\text{-}Bu_2NH_2)_2SnCl_6$	5.9	2	10	434	−1404	1069	1261
13	$(n\text{-}Bu_3NH)_2SnCl_6$	5.5	2	10	355	−1456	935	1150
14	$(n\text{-}Bu_4N)_2SnCl_6$				(286)	(−1511) −1527	(814)	1127
15	$(i\text{-}BuNH_3)_2SnCl_6$			10	407	−1261	1112	1294
16	$(s\text{-}BuNH_3)_2SnCl_6$		2	10	461	−1327	1158	1290
17	$(t\text{-}BuNH_3)_2SnCl_6$			10	419	−1317	1108	1271
18	$(i\text{-}Bu_2NH_2)_2SnCl_6$	6.6		10	486	−1501	1116	1246
19	$(i\text{-}PentNH_3)_2SnCl_6$	7.0	2	10	518	−1417	1220	1294
20	$(c\text{-}HexNH_3)_2SnCl_6$	6.5	4	10	429	−1296	1121	1290
21	$(PyrH)_2SnCl_6$	6.8		10	464	−1127	1130	1267
22	$(PipH)_2SnCl_6$			10	391	−1145	1048	1277

[a] Values obtained by extrapolation are given in parentheses. [b] Values underlined were determined from eqn. (7) using values of the crystal lattice energy estimated by extrapolation (column A of this table) and values of the enthalpy of formation of the quaternary alkanaminium ions from ref. 16. [c] Values obtained from the thermochemical cycle. [d] Values estimated from the Kapustinskii–Yatsimirskii formula (eqn. (9)).

where $\Delta H_v^\ominus$ is the enthalpy of volatilization derived from the thermogravimetric investigations (Table 3) and $\Delta H_{fn}^\ominus$ is the enthalpy of fusion. The term $\Sigma\ \Delta H_\sigma^\ominus$ arises from any polymorphic transitions which these compounds may undergo between 298 K and the onset of volatilization. The term $\int_{298}^{T} \Delta C_p^\ominus\ \mathrm{d}T$ accounts for the change in enthalpy resulting from changes in heat capacities of the reactants. Since the pertinent data for $\Delta H_{fn}^\ominus$ are not available, we estimated the values of this quantity using an empirical relationship with the entropy of fusion $\Delta S_{fn}^\ominus = \Delta H_{fn}^\ominus / T_m =$ constant. The entropies of fusion have not been reported as yet for the alkanaminium hexachlorostannates studied here. The available data for NH_4NO_3 [26] suggest that $\Delta S_{fn}^\ominus$ for the compound is ca. 14 J mol^{-1} K^{-1}. On the basis of information in the literature for mono-*n*-alkanaminium chlorides [27,28] we estimated $\Delta S_{fn}^\ominus$ to be 13.6 J mol^{-1} K^{-1} in our earlier studies [16,20]. We have assumed that this value for the entropy of fusion is adequate for all alkanaminium hexachlorostannates. Taking this value and the temperatures of melting from Table 2 we derived values of $\Delta H_{fn}^\ominus$ for the compounds 7, 8, 11, 12, 13, 18, 19, 20 and 21. They are listed in Table 5. For compounds 1, 2, 4, 5, 10, 15, 16, 17 and 22 the term $\Delta H_{fn}^\ominus$ was neglected, since these compounds melt and decompose simultaneously ($T_m > T_{0.08}$) and the process of fusion probably does not affect the thermodynamics of dissociation of these derivatives.

Some of the compounds studied undergo solid phase transitions (Table 2). Unfortunately, the pertinent data for $\Delta H_\sigma^\ominus$ are not available. Such transitions usually amount to a few kilojoules per mole. For example, for alkanaminium chlorides a value of ca. 4 kJ mol^{-1} has been reported [16,20,27]. Matsuo et al. [29] have estimated that the enthalpy of the phase transition for methylammonium hexachlorostannate is ca. 2 kJ mol^{-1}. This value was used for each phase transition occurring in the compounds examined (Table 5).

The magnitude and sign of the heat capacity term is also difficult to estimate in the absence of heat capacity data for hexachlorostannates and their decomposition fragments. In ref. 1, we demonstrated that the heat capacity term for the sublimation of $(NH_4)_2SnCl_6$ is ca. -10 kJ mol^{-1}. This value was assumed in this work to account for the changes in enthalpy of volatilization resulting from the changes in heat capacity of the reactants (Table 5). At least two facts may justify such an assumption. Firstly, volatilization of alkanaminium hexachlorostannates proceeds over a temperature range similar to that for the sublimation of $(NH_4)_2SnCl_6$. Secondly, the expected changes in heat capacity brought about by an increase in the size of the alkyl group should be identical for salts and for the corresponding amines. Thus the change in size and structure of the alkyl groups, as well as the number of substituents, may not influence $\Delta C_p^\ominus$.

On the basis of the above considerations we modified the values of $\Delta H_v^\ominus$, and these are listed in Table 5. To evaluate the thermochemical quantities

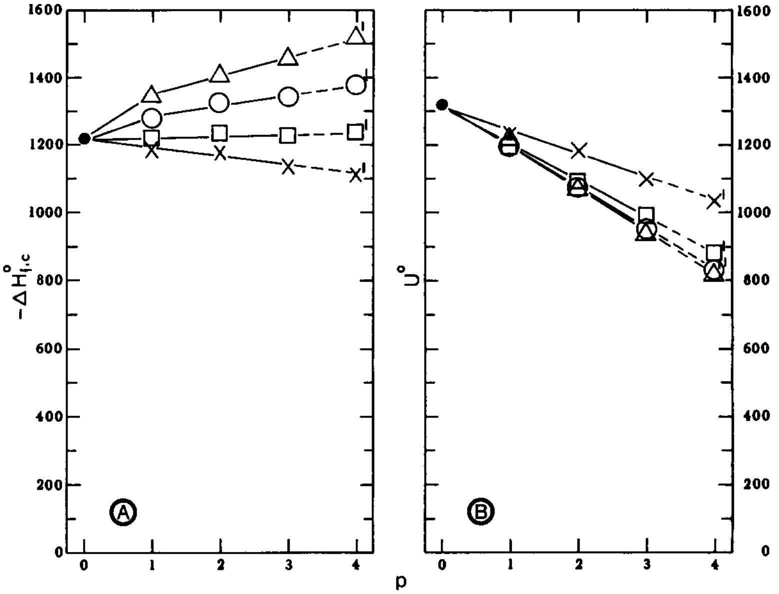

Fig. 2. The enthalpies of formation (A) and crystal lattice energies (B) (both in kJ mol^{-1}) for $(A_pNH_{4-p})_2SnCl_6$ vs. the number of alkyl groups p: ●, A = H; ×, A = Me; □, A = Et; ○, A = n-Pr; △, A = n-Bu; values with a comma were obtained by extrapolation.

from eqns. (6) and (7) we used values of the enthalpies of formation of the gaseous amines and the appropriate alkanaminium cations from refs. 11 and 16. Furthermore, values of $\Delta H^{\ominus}_{f,g}[HCl]$, $\Delta H^{\ominus}_{f,g}[SnCl_4]$ and $\Delta H^{\ominus}_{f,g}[SnCl_6^{2-}]$ were assumed to be equal to (in kJ mol^{-1}) -92.3 [30], -472 [30] and -1156 [31], respectively. The derived $\Delta H^{\ominus}_{f,c}$ and $U^{\ominus}$ values for the primary, secondary and tertiary alkanaminium hexachlorostannates studied are shown in Table 5.

The crystal lattice energies and enthalpies of formation of the alkanaminium hexachlorostannates are characteristic for a given compound. A close inspection of the values of both the above quantities for unbranched alkanaminium hexachlorostannates with the general formula $(A_pNH_{4-p})_2$-$SnCl_6$ indicates an interesting dependence on the number of substituents (A). To demonstrate this dependence values of $\Delta H^{\ominus}_{f,c}$ and $U^{\ominus}$ derived in this work (Table 5) are plotted in Fig. 2 together with the appropriate data taken from ref. 1 (the enthalpies of formation of mono-n-alkanaminium hexachlorostannates from our previous work were modified using more reliable data for the enthalpies of formation of amines [11,32,33]. Figure 2(B) demonstrates that the crystal lattice energies of these derivatives decrease linearly with the number of A groups in the amine molecule; this tendency is observed in the range $p = 0$–3. By assuming that an analogous trend is valid for $p = 4$ we can obtain the values of the crystal lattice energy for the quaternary salts by extrapolation (Table 5). An examination of the values of the enthalpies of formation reveals that the linear dependence of this quantity on p is actually observed only for the methyl- and ethyl-substituted derivatives (Fig. 2(A)). For n-Pr- and n-Bu-substituted compounds the linear dependence holds in the range $p = 1-3$. The $\Delta H_{f,c}^{\ominus}$ values for the quaternary salts can thus be estimated by extrapolation as above. The values of this quantity are given in Table 5. We also calculated the values of $\Delta H_{f,c}^{\ominus}$ for quaternary salts from eqn. (7) using the extrapolated values of $U^{\ominus}$ and the values of the enthalpy of formation of the appropriate alkanaminium cations from our previous work [16]. As shown in Table 5, the agreement between these derived values of $\Delta H_{f,c}^{\ominus}$ and those obtained by extrapolation is quite good. This strengthens the reliability of the thermochemical characteristics determined by us. Moreover, this indicates that the basic thermochemical characteristics of alkanaminium salts are additive.

To complete the information obtained on the thermochemistry of alkanaminium hexachlorostannates we also estimated values of $\Delta H_{v}^{\ominus}$ for quaternary salts on the basis of eqn. (6). For this purpose we used values of $\Delta H_{f,c}^{\ominus}[(A_4N)_2SnCl_6]$ obtained by extrapolation. Furthermore, values of $\Delta H_{f,g}^{\ominus}[MeCl]$, $\Delta H_{f,g}^{\ominus}[EtCl]$, $\Delta H_{f,g}^{\ominus}[n\text{-}PrCl]$ and $\Delta H_{f,g}^{\ominus}[n\text{-}BuCl]$ were assumed to be equal to (in kJ mol^{-1}) -82.0, -112.1, -132.4 and -154.5, respectively [32]. The estimated enthalpies of the thermal decomposition are listed in Table 5. On reviewing the values of this quantity for all the alkanaminium hexachlorostannates studied in this and in our previous work [1] it can be seen that $\Delta H_{v}^{\ominus}$ decreases with an increase in size of the alkyl group and an increase in number of the substituents. A slight dependence of $\Delta H_{v}^{\ominus}$ on the structure of the alkyl group is also observed. This dependence is not strongly pronounced and, at present, no conclusions can be drawn.

To shed more light on the thermochemistry of the compounds examined we also considered the crystal lattice energy using the Kapustinskii–Yatsimirskii equation [34,35]

$$U = 120.2\frac{(\Sigma n)Z_K Z_A}{r_K + r_A}\left[1 - \frac{0.0345}{r_K + r_A} + 0.087(r_K + r_A)\right] (\text{kJ mol}^{-1}) \qquad (9)$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule, Z_K and Z_A are the numerical values of the charges of the cation and anion, respectively and r_K and r_A are the "thermochemical" ionic radii (in nm). To use the above equation, the "thermochemical" radii for cations and anions are required. The values of r_K for alkanaminium cations were taken from our previous work [1,11,16]. These values were obtained by the examination of the thermochemistry of alkanaminium chlorides. For $r_{SnCl_6^{2-}}$ we assumed a value equal to 0.370 nm. This value was obtained from eqn. (9) using the available data for the crystal lattice energies of alkali metal hexachlorostannates [31] and the appropriate radii of the cations from ref. 36. The value obtained for the "thermochemical" radius of $SnCl_6^{2-}$ differs somewhat from that suggested elsewhere by Jenkins and Thakur [37] (i.e.

0.349 nm). However, in our case a value of 0.37 nm for $r_{SnCl_6^{2-}}$ seems to be more adequate. The values of U obtained using eqn. (9) are listed in Table 5. The comparison of these values of U (Table 5, column B) with those obtained from the thermochemical cycle (Table 5, column A) shows very poor agreement, although both these sets of data show similar dependence on the size and structure of the alkyl group, as well as on the number of substituents at the nitrogen atom.

CONCLUDING REMARKS

Thermoanalytical methods are very useful in the examination of the thermal properties, kinetics of thermolysis and thermochemistry of compounds. The last two subjects can only be examined if the processes which occur on heating are not complex.

Two basic thermochemical characteristics of alkanaminium hexachlorostannates, i.e., the enthalpies of formation and the crystal lattice energies, were derived from the thermochemical cycle using directly determined enthalpies of thermal dissociation of the compounds. The values of $\Delta H_{f,c}^{\ominus}$ and $U^{\ominus}$ for the alkanaminium hexachlorostannates depend on the size and structure of the alkanaminium cation (in a similar manner to the chlorides). This is particularly pronounced in the series of derivatives with various numbers of unbranched alkyl substituents in the aminium cation (see ref. 16, Fig. 2 and Fig. 2 of this work). This and other information on the thermochemistry of alkanaminium salts reveals that both $\Delta H_{f,c}^{\ominus}$ and $U^{\ominus}$ are additive.

From Table 5 it can be seen that the values of U calculated using the Kapustinskii–Yatsimirskii formula are markedly higher than those evaluated from the thermochemical cycle. Such disagreement may result from an incorrect choice of values of the "thermochemical" radii. As mentioned earlier values of r_K were derived from the known crystal lattice energies of the appropriate chloride salts. Therefore, the results of this work clearly demonstrate that the Kapustinskii–Yatsimirskii approach does not apply to salts of highly unsymmetrical ions. For such ions "thermochemical" radii are not additive. Further insight into this problem will be gained when the phenomenological basis is extended.

The comparison of the influence of the size and structure of the alkanaminium cation on the crystal lattice energies of the chlorides and the corresponding hexachlorostannate salts reveals that in the latter case the effect is much more pronounced. The crystal lattice energy of ionic crystals is affected mainly by the coulombic interaction between charged centres. The crystallographic investigations on alkanaminium chlorides revealed that the linear hydrogen bond $\geqslant$N–H $\cdots$ Cl, whose distance is affected only insignificantly by the alkyl groups attached to nitrogen, plays an important role in the structure of these compounds [38–40]. Because the charged centres in these derivatives are located on nitrogen and chlorine atoms similar values for the crystal lattice energies of these derivatives can be expected. The crystal structures of aminium hexachlorostannates consist of a simple structural unit of octahedral $SnCl_6^{2-}$ connected with two aminium cations by a bifurcated hydrogen bond [10,41,42]. In this case the separation of charged centres should be more affected by the environment than in the case of a linear hydrogen bond. Therefore, the crystal lattice energies of hexachlorostannates should depend significantly on the structural changes in the molecules; this is fully supported by the results of our investigations.

Undoubtedly, to complete the crystal lattice energy examination it would be useful to calculate the crystal lattice energies of the compounds using lattice parameters. This is currently being undertaken.

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