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THERMOCHEMICAL PROPERTIES OF H_2SnCl_6 COMPLEXES. PART I. THERMAL BEHAVIOUR OF PRIMARY *n*-ALKYLAMMONIUM HEXACHLOROSTANNATES *

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ABSTRACT

Thermogravimetry and differential thermal analysis have been applied to the investigation of the thermal behaviour of mono-*n*-alkylammonium hexachlorostannates of general formula $(C_nH_{2n+1}NH_3)_2SnCl_6$, with $n = 0–8$. Irrespective of the chain-length, the thermal dissociation of the salts occurs in one step and leads to their total volatilization. The thermal analysis curves were used for examination of the thermodynamics and kinetics of this process.

The values evaluated for the enthalpy of volatilization enable the estimation of the enthalpy of formation and the energy of the crystal lattice of the salts from the thermochemical cycle. The crystal lattice energies of the compounds were also evaluated on the basis of the Kapustinskii–Yatsimirskii equation. The latter values remain in good agreement with those resulting from the thermochemical cycle.

The Jacobs and Russell-Jones theory was applied to the examination of the kinetics of volatilization. This model also explains the existence of two stages for the process, which were actually seen on TG curves of all the compounds studied. The values of the apparent activation energy derived on the basis of this theory are very close to the values of the enthalpy of volatilization. On the other hand, assuming that the kinetics follow the zero kinetic order equation or the contracting surface area law, more than 4 times lower values of apparent activation energy were obtained. The explanation of these discrepancies is given.

INTRODUCTION

The tetrachlorides of the main group IV elements have received much attention in the past owing to their interesting physical and chemical properties (Table 1) [1,2]. $M^{IV}Cl_4$ (M^{IV} = C, Si, Ge, Sn, Pb) have tetrahedral structure [7,8]. Under normal conditions they are liquids of relatively high densities. They are also easily soluble in a number of organic solvents. Although they are compounds with high molecular weights their melting and boiling points are fairly low, as a result of their non-polar structure. The

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TABLE 1

Selected physical and chemical characteristics of the main group IV chlorides

Compound	M.p. [3] (K)	B.p. [3] (K)	Density [3] ($g\,cm^{-3}$)	$\Delta H^0_{f,298}$ ($kJ\,mol^{-1}$)	ΔH^0_{298} ($kJ\,mol^{-1}$) for the reaction $M^{IV}Cl_4 \rightarrow M^{II}Cl_2 + Cl_2$
$CCl_{4(l)}$	250.1	350.0	1.5867	−135 [3]	374
$SiCl_{4(l)}$	203.2	330.7	1.483	−687 [3]	527
$GeCl_{4(l)}$	223.6	357.1	1.8443	−532 [3]	313
$SnCl_{4(l)}$	240.2	387.2	2.226	−511 [3]	185
$PbCl_{4(l)}$	258.1	expl.	3.18	−329 [3]	−31
$CCl_{2(g)}$				239 [3]	
$SiCl_{2(g)}$				−160 [5]	
$GeCl_{2(g)}$				−219 [6]	
$SnCl_{2(c)}$	519	925	3.95	−325 [3]	
$PbCl_{2(c)}$	774	1223	5.85	−360 [3]	
$GeCl_{6(g)}^{2-}$				−981 [4]	
$SnCl_{6(g)}^{2-}$				−1156 [4]	
$PbCl_{6(g)}^{2-}$				−940 [4]	

tetrachlorides of group IVA exhibit distinct electron-acceptor properties [9–14]. This behaviour of the $M^{IV}Cl_4$ compounds is due to the fact that the central atoms of most of them have formally empty *d* orbitals [13,15]. The exception is CCl_4 whose electron-acceptor properties are mainly of a different nature [13,16], since *d* orbitals are not accessible in the valence shell of the carbon atom. Because of these interesting properties, $M^{IV}Cl_4$ compounds have often been applied as model compounds for investigations of EDA interactions [12,13]. The tetrachlorides of the elements at the edges of the IV A group, namely CCl_4 and $PbCl_4$, show slightly different behaviour as compared with those within the IVA group, namely $SiCl_4$, $GeCl_4$ and $SnCl_4$. Carbon tetrachloride is the weakest electron-acceptor among $M^{IV}Cl_4$ compounds, moreover, it does not form the complex CCl_6^{2-} ion. The existence of $SiCl_6^{2-}$ is uncertain [17], instead, germanium, tin and lead form stable complex ions of the type $M^{IV}Cl_6^{2-}$. The electron-acceptor properties of $M^{IV}Cl_4$ become stronger for the heavier elements of the group. $PbCl_4$, which has the most distinct electron-acceptor properties, is thermodynamically unstable (Table 1) [18]. Lead tetrachloride easily undergoes the intermolecular redox reaction which is caused by the relatively high Pb^{4+}/Pb^{2+} potential (+1.5 V [19]) in comparison with that of $Cl_2/2\,Cl^-$ (+1.36 V [3]). This feature of $PbCl_4$ calls our attention and provokes us to investigate the thermal properties of its molecular complexes [20–24]. On the one hand, this behaviour of lead tetrachloride enables the examination of certain types of reactions proceeding in the solid phase upon heating, but on the other hand, it complicates the course of thermolyses of its molecular complexes with organic precursors, since chlorination processes may occur [20–22,24]. For a better understanding of the thermal properties of molecular complexes of tetrachlorides of the main group IV elements it seems to be necessary to extend the investigations of derivatives formed with $M^{IV}Cl_4$ compounds other than $PbCl_4$. Tin tetrachloride seems to meet the best criteria for the model compound. $SnCl_4$ can be easily obtained and is also easy to work with in the laboratory. The electron-acceptor properties of $SnCl_4$ are comparable with those of $PbCl_4$, however, owing to the relatively low Sn^{4+}/Sn^{2+} potential (+0.15 V [19]) tin tetrachloride does not decompose spontaneously to $SnCl_{2(c)}$ and $Cl_{2(g)}$ (Table 1). It is also worth mentioning that both tin and lead form stable divalent chlorides.

This paper is the first of a series and is devoted to the thermal behaviour of primary *n*-alkylammonium hexachlorostannates. Knowledge of the thermal properties of this group of compounds is scattered and fragmentary [4,25–33] although numerous other of their properties have been established on the basis of X-ray [34–38] and neutron diffraction [36,39] measurements, as well as, IR [37,40–45], Raman [41,43,46,47], NMR [29,48,49], NQR [29,50–53], ESR [54], UV [32,55], Mössbauer [46,56,57] and MCD [58] spectroscopic investigations. Knowledge of the thermochemistry of these compounds is also of considerable practical importance.

EXPERIMENTAL

Ammonia and amines of pure grade were used as received [24]. Other reagents of analytical grade have been used throughout. The ammonium and alkylammonium hexachlorostannates were prepared by literature methods [59,60]. The purity of the compounds was checked by elementary analysis.

TABLE 2

Temperatures corresponding to a certain extent of dissociation for $[CH_3(CH_2)_2NH_3]_2SnCl_6$ and $[CH_3(CH_2)_6NH_3]_2SnCl_6$ (see Fig. 1)

α	Temperature (K)	
	$[CH_3(CH_2)_2NH_3]_2SnCl_6$	$[CH_3(CH_2)_6NH_3]_2SnCl_6$
0.1	518.1	521.4
0.18	532.9	537.1
0.26	542.0	545.8
0.34	549.1	553.3
0.42	554.2	558.9
0.50	559.1	564.5
0.58	562.9	568.3
0.66	566.7	572.4
0.74	570.8	575.0
0.82	574.0	

The thermal analyses were performed 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 [61] (Appendix 1, No. 4). Other operating conditions are given in Table 3.

The temperature (T) values corresponding to certain values of the degree of conversion (α) were determined using experimental curves in a manner described previously [23,24]. For each compound, the set of experimental data points, used in further calculations, was taken as a mean from at least three replicate measurements. An example is given in Table 2.

RESULTS

The thermal analysis runs recorded by a derivatograph for two compounds chosen as an example and shown in Fig. 1 are typical for all the compounds studied. The essential parameters characterizing the thermal behaviour of this group of compounds, derived from thermal analysis curves, are compiled in Table 3.

The general feature of thermolysis of mono-*n*-alkylammonium hexachlorostannates is that they undergo total volatilization upon heating to 700 K. Only in the case of long-chain alkylammonium salts (n = 6–8) is a minor

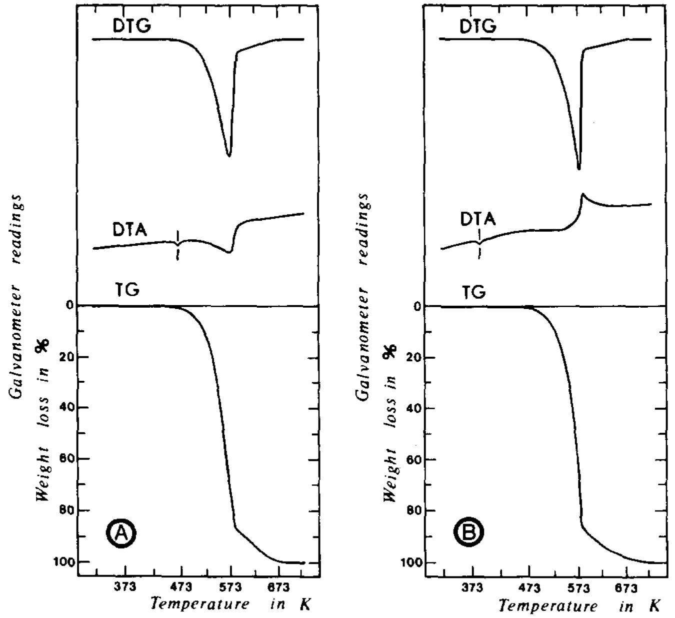


Fig. 1. Thermal analyses of $[CH_3(CH_2)_2NH_3]_2SnCl_6$ (A) and $[CH_3(CH_2)_6NH_3]_2SnCl_6$ (B).

TABLE 3

The thermal analyses of mono-*n*-alkylammonium hexachlorostannates [a]

Data No.	Substance $(C_nH_{2n+1}NH_3)_2SnCl_6$ $n =$	Φ (K min^{-1})	Sample weight (mg)	Peak temperature [b] (K)					Temperature [b] (K)			Parameters describing the beginning of the second stage	
				DTG	DTA				$T_{0.1}$	$T_{0.82}$	$\Delta T_\alpha = T_{0.82} - T_{0.1}$	α	T (K)
					T_σ		T_p						
						From literature	endo	exo					
1	0	4.9	50	570			575		515.2	572.6	57.4	0.92	582
2		0.83	100	543					493.2	546.9	53.7	0.89	552
3		2.4	100	561			562		508.9	566.4	57.5	0.91	574
4		5	100	581			584		525.9	585.7	59.8	0.92	595
5		10	100	610			622		550.5	617.6	67.1	0.90	629
6		20	100	625			638		552.5	634.7	82.2	0.92	649
7		5.7	300	612			614		547.4	612.4	65.0	0.92	620
8	1	4.9	100	588			591		535.0	594.2	59.2	0.86	598
9	2	5	100	578			581		523.2	582.9	59.7	0.86	586
10	3	5	100	570	468	467 [62]	572		518.2	574.0	55.8	0.87	582
11	4	5	100	572			574		523.7	578.4	54.7	0.86	583
12	5	4.8	100	572	499				522.4	574.5	52.1	0.87	578
13	6	5	100	574	400			588				0.83 [c]	578 [c]
14	7	4.7	100	576	384			587				0.82 [c]	579 [c]
15	8	4.8	100	569	353			581				0.76 [c]	573 [c]

[a] Sensitivities of galvanometers were: 1/10 or 1/20 for DTG; 1/2, 1/3 or 1/5 for DTA; and 50, 100 or 500 mg for TG.

[b] The symbols were taken from ref. 63. T_p = temperature of the peak, T_σ = temperature of a solid-state phase transition and T_α = temperature at which the degree of conversion is equal to α (i.e., $T_{0.1} = T_{\alpha=0.1}$).

[c] Participation of side processes.

participation of side reactions observed. It is, however, interesting that two distinct stages are always seen in TG curves (Fig. 1). The first fast step, in which up to 92% of the sample volatilizes, is followed by a slow one, seen as a "tail", in which the remaining part of the sample disappears. The occurrence of this effect results from the mechanism of the volatilization process, which will be discussed subsequently.

The standard capillary method proved that none of the compounds studied melted before the onset of volatilization. Thus, the endothermic peaks seen in DTA curves below the temperature of the onset of the process can be ascribed to the phase transitions. To our knowledge only the phase transition for *n*-propylammonium hexachlorostannate has been so far reported in the literature [62]. It is, however, worth mentioning that compounds with $n = 0$–2 undergo various phase transformations below the ambient temperature [29,30,33,37,51,64]. Unfortunately, these transitions could not be detected with the method applied.

The characteristic temperatures, namely, T_p (from DTA and DTG curves), as well as $T_{0.1}$, $T_{0.82}$ and ΔT_α show a slight dependence on the length of the aliphatic chain of the amine. It is worth noting that similar regularities have been observed for mono-*n*-alkylammonium chlorides [65] and hexachloroplumbates [24], however, T_p, $T_{0.1}$ and $T_{0.82}$ attain markedly higher values in the case of the compounds examined.

The values of peak temperatures in DTA are always a few degrees higher than the corresponding peaks in DTG. Similar regularities have been observed earlier upon thermoanalytical examinations of hexachloroplumbates [20–24] and amine hydrochlorides [65]. The increase in the values of characteristic temperatures of the thermal decomposition with both mass of the sample and heating rate is a phenomenon typical for thermoanalytical investigations [66].

DISCUSSION

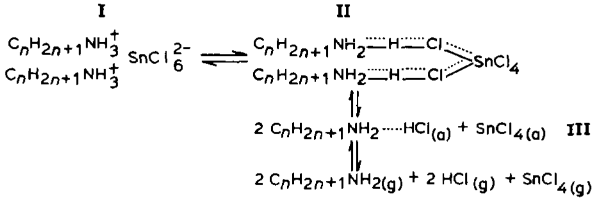
General nature of the decomposition process

There are only a few reports concerning thermal decomposition of ammonium hexachlorostannate [26,67–69], however, none of them touch on the problem of the mechanism of the process. By analogy to the thermal behaviour of other ammonium salts [65,70–77] the thermal decomposition of the compounds studied can be considered as a typical dissociative sublimation process which can be summarized by the equation

$$(C_nH_{2n+1}NH_3)_2SnCl_{6(c)} \rightarrow 2\ C_nH_{2n+1}NH_{2(g)} + 2\ HCl_{(g)} + SnCl_{4(g)} \qquad (1)$$

The dissociation of alkylammonium hexachlorostannates proceeds far above the boiling points of the appropriate amines, $SnCl_4$ and HCl [3], and thus, all the products should appear in the gaseous phase. It is not, however, known a priori whether products formed behave as kinetically free fragments in the gas phase or whether they interact with each other forming aggregates. The formation of weak complexes between amines and HCl can be expected on the basis of theoretical considerations [78,79], as well as certain experimental evidences [80,81]. The interaction between amines and $SnCl_4$ is even less likely [82]. On the other hand, HCl and $SnCl_4$ presumably do not interact with each other as both exhibit electron-acceptor properties. The above considerations clearly indicate that eqn. (1) is oversimplified. Nonetheless, it forms a convenient framework for further thermochemical and kinetic considerations.

The full mechanism of the volatilization of alkylammonium hexachlorostannates is, undoubtedly, much more complicated than shown by the simple eqn. (1). Numerous similarities in the thermal behaviour of the compounds studied and other ammonium salts [65,70,72–74,76], allow one to admit that the mechanism of the sublimation process is essentially the same. On the basis of the current knowledge of the problem we propose the following mechanism for the process:



(2)

At least three stages are involved in the volatilization of $(C_nH_{2n+1}NH_3)_2SnCl_6$, namely: (i) proton transfer in the ion triple (from 2 $C_nH_{2n+1}NH_3^+$ to $SnCl_6^{2-}$) being at a position of a half-crystal site (I) which leads to the creation of the transition state (II); (ii) dissociation of the molecule in the transition state followed by formation of mobile adsorbed phase (III); and (iii) desorption of the adsorbed molecules from the surface. The migration of the molecules over the surface followed by their diffusion through the gas phase represents the sublimation process.

Thermodynamics of the thermal decomposition

The enthalpy of sublimation (ΔH_s) was evaluated on the basis of the Van't Hoff equation. The volatilization of 1 mole of alkylammonium hexachlorostannate results in the formation of 5 moles of gaseous products. Hence, based on our previous considerations [23], ΔH_s can be derived from the equation

$$\ln \alpha = -\frac{\Delta H_s}{5R}\frac{1}{T} + \text{const.} \tag{3}$$

where R is the gas constant.

The values evaluated for the enthalpy of sublimation are listed in Table 4. Only in the case of ammonium hexachlorostannate can values thus derived be compared with those reported in the literature. The agreement is quite good considering the variety of sources from which they have been drawn.

The derived values of ΔH_s depend somewhat on the size of the alkyl substituent, although differences observed are small and they may be ascribed, in part, to the experimental uncertainties. Nevertheless, the gradual increase of the values of ΔH_s with the increase of the length of the alkyl substituent can be seen. It may also be noticed that the changes in mass of the sample analysed do not affect the derived values of ΔH_s. On the other hand, use of the experimental TG curves recorded at high heating rates for

TABLE 4

Enthalpies of sublimation of primary *n*-alkylammonium hexachlorostannates [a]

Data No.	Substance $(C_nH_{2n+1}NH_3)_2SnCl_6$ $n =$	Const.	ΔH_s (kJ mol^{-1})	Enthalpy of volatilization (kJ mol^{-1})	
				From literature [b]	Calculated on the basis of the standard enthalpy of formation at 298 K [f]
1	0	18.9	454	612.6 (503–644) [26] [c]	532 *
2		19.4	444	609.0 (503–644) [d]	488 **
3		18.7	443	412.2 (527–618) [67] [e]	495.3 ***
4		18.7	459		
5		17.5	452		
6		14.3	380		
7		17.6	453		
8	1	19.0	474		
9	2	18.7	457		
10	3	19.6	471		
11	4	20.5	496		
12	5	21.1	508		
13	6	19.8	481		
14	7	19.1	465		
15	8	21.0	506		

[a] Values of ΔH_s and const. were calculated from eqn. (3), within a range of α from 0.1 to 0.82 (for $n = 0$–5); to 0.74 (for $n = 6, 7$); and to 0.66 (for $n = 8$).

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

[c] The authors originally derived for ΔH_s value equal to 122.5 kJ mol^{-1}. They assumed, however, that $(NH_4)_2SnCl_6$ molecule is transferred from the solid to the gas phase without decomposition. According to eqns. (1) and (3) this value should be multiplied by 5.

[d] Values derived on the basis of eqn. (3) using $p = f(T)$ data from ref. 26.

[e] ΔH_s value was taken from ref. 69, pp. 98 and 99.

[f] Values used in the calculations (kJ mol^{-1}): $\Delta H^0_{f,g}[HCl] = -92.3$ [3]; $\Delta H^0_{f,g}[NH_3] = -46.1$ [3]; $\Delta H^0_{f,g}[SnCl_4] = -472$ [83]; $\Delta H^0_{f,c}[(NH_4)_2SnCl_6] = -1281$ [25] *, -1237 [83] ** and -1244.1 [31] ***.

the evaluation of the enthalpy change for the process does not seem to be adequate.

Kinetics of volatilization

In the search for an adequate method describing the kinetics of the dissociative sublimation process one comes to the conclusion that none of the approaches to the problem proposed in the past [70,71,73,74,76,77,84,85] can be accepted without reservations. During the study of the volatilization of alkylammonium chlorides we found that the surface diffusion model, originally proposed by Jacobs and Russell-Jones [73], satisfactorily describes the kinetics of non-isothermal dissociation of these compounds [65]. A detailed discussion of this method, as well as its adaptation to non-isothermal conditions, have been given in our previous work [65]. Below we present the final form of the integral equation describing the kinetics of volatilization of the compounds studied at linearly increasing temperature.

$$\left(X_2T-\frac{\Delta}{a_0}\right)\left[1-(1-\alpha)^{1/3}\right]+\tfrac{1}{2}\left[1-(1-\alpha)^{2/3}\right]$$
$$-\left(\frac{\Delta}{a_0}\right)^2\ln\left[\frac{(1-\alpha)^{1/3}+\Delta/a_0}{1+\Delta/a_0}\right]=\frac{1}{3}\frac{X_1}{\Phi}T^{3/2}\mathrm{e}^{-E/5RT} \qquad (4)$$

where X_1, X_2 and E are the constants and E can be identified with the activation energy for the process, Φ is the heating rate, a_0 represents the initial radius of particles from which the sublimation process occurs and Δ denotes the distance between collisions (i.e., a distance which a molecule travels after leaving the condensed phase, before a collision occurs). Since at moderate pressures of a foreign gas, $P \approx$ atmospheric pressure, $\Delta \ll a_0$, the influence of this parameter on the kinetics of sublimation is negligibly small, then eqn. (4) can be simplified to the form

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

Another approach which we intend to invoke in this work is that which the process of volatilization of alkylammonium salts considers as a reaction proceeding on the surface of the solid phase [73]. Then the kinetics should follow the contracting surface area law.

$$1-(1-\alpha)^{1/2}=Z\frac{T}{\Phi}\mathrm{e}^{-E^*/RT} \qquad (6)$$

where Z and E^* are the constants from the Arrhenius equation and E^* identifies with the activation energy for the process. Equation (6) has been derived assuming that the degree of conversion is a function of both time and temperature [86]. Starting from the Jacobs and Russell-Jones equation

[73] and making various simplifications, Naumova et al. [87] also obtained the contracting surface area equation for describing the kinetics of sublimation under non-isothermal conditions.

Kinetic constants derived on the basis of both the above methods are compiled in Table 5. Application of the Jacobs and Russell-Jones equation leads to values of E slightly lower than the appropriate values of the enthalpy of volatilization and this fact remains in accordance with the well-known physical significance of this magnitude. It is also worth mentioning that similar regularities have been observed upon volatilization of alkylammonium chlorides [65]. The meaning of X_1 and X_2 constants is not defined precisely. It is, however, known that both parameters should be

TABLE 5

Kinetic constants for dissociation of mono-n-alkylammonium hexachlorostannates

Data No.	Substance $(C_nH_{2n+1}NH_3)_2SnCl_6$ $n =$	Methods of treatment				
		Jacobs and Russell-Jones, eqn. (5) [a,b]			Contracting surface area model, eqn. (6) [a,c]	
		X_1 $(1/(K^{1/2}s))$	X_2 (1/K)	E (kJ mol^{-1})	Z (1/s)	E^* (kJ mol^{-1})
1	0	625	-1.7×10^{-4}	442	9.1×10^{4}	99.2
2		190	-2.8×10^{-4}	436	2.6×10^{4}	97.0
3		308	-2.1×10^{-4}	438	3.3×10^{4}	96.7
4		142	-4.6×10^{-4}	423	6.9×10^{4}	100
5		77	-3.6×10^{-4}	412	3.3×10^{4}	98.4
6		8.6	-2.5×10^{-4}	346	1.7×10^{3}	81.9
7		97	-3.8×10^{-4}	430	2.2×10^{4}	98.6
8	1	1220	2.5×10^{-5}	473	1.0×10^{5}	104
9	2	352	-4.6×10^{-4}	443	6.5×10^{4}	99.6
10	3	1630	-3.2×10^{-4}	469	1.9×10^{5}	103
11	4	1430	-3.5×10^{-4}	470	5.5×10^{5}	109
12	5	8770	-2.1×10^{-4}	508	1.1×10^{6}	112
13	6	270	-7.5×10^{-4}	444	1.5×10^{5}	103
14	7	52	-7.8×10^{-4}	405	6.9×10^{4}	100
15	8	6.7	-1.2×10^{-3}	370	3.8×10^{5}	107

[a] Values of kinetic constants were evaluated on the basis of the experimental $\alpha = f(T)$ dependencies, within a range of α from 0.1 to 0.82, for $n = 0$–5; to 0.74, for $n = 6$, 7; and to 0.66, for $n = 8$.

[b] Values of X_1, X_2 and E were derived using least squares procedure described in ref. 65. There are, however, some errors in the description of this procedure. Equations (A7) and (A8) are both incorrect. δ function should be expressed with the equation:

$$\delta = \left| X_2 \sum \frac{A_iC_i}{T_i} + \frac{1}{2}\sum \frac{B_iC_i}{T_i} - \frac{X_1}{3\Phi}\sum \frac{C_i^2}{T_i} \right|$$

[c] Values of Z and E * were calculated on the basis of the standard least squares method (see ref. 24, eqn. 9).

positive. Unfortunately, most of the derived values of X_2 are negative. One possible explanation of this fact might be that it results from neglecting the term Δ/a_0 in eqn. (5), being formally negative (see eqn. 4). On the other hand, values of X_2 are very low and this means that the first term in eqn. (5) does not significantly influence the kinetics of the process. The above facts clearly show that both X_1 and X_2 should be considered rather as mathematical constants without true physical significance.

Despite some criticism of the Jacobs and Russell-Jones model [74] one fact remains unquestionable. This is the only model which gives a qualitative explanation for the existence of two stages in the volatilization process of liquid and solid substances, which are actually seen on the TG curves of the compounds studied. As it has been pointed out earlier the term Δ/a_0 in eqn. (4) is negligibly small in our experimental conditions and can be neglected. However, at the end of the volatilization process the geometric surface area of the condensed phase decreases and Δ increases. It causes a gradual decrease of the rate of the process as both terms containing Δ/a_0 are negative.

It is much more difficult, however, to account for the very low values of apparent activation energy derived from eqn. (6). Moreover, yet lower activation energy values were derived assuming that the process obeys the Polanyi–Wigner equation, i.e., zero kinetic order equation. The latter method was very often proposed in the past for describing the kinetics of sublimation of ammonium salts [70–72,75,76].

To comment on these facts one has to remember the condition which justifies the use of the Arrhenius equation. That is, that the whole process has only one step which determines its kinetics, or in other words, a "bottleneck" exists for the process. It is, therefore, difficult to imagine that the molecule can reach a high energy level resulting from ΔH_s in only few steps if one of them, the rate determining step, has an energy barrier for activation equal to ca. 1/4 of the ΔH_s value. If the whole sublimation process indeed proceeds as a sequence of consecutive steps, the use of the Arrhenius equation does not seem to be adequate, especially if one intends to ascribe physical significance to thus derived values of apparent activation energy.

On the other hand, one can notice that the Arrhenius equation (i.e., eqn. (6)) fits the experimental data surprisingly well. It would mean that a rate determining step actually exists for the process. In search for an explanation supporting this conception we could not resist the impression that some mathematical changes introduced into the classical Arrhenius equation would make it more realistic. To find the basis for such changes one has to reconsider the physical meaning of apparent activation energy. Generally, E describes the energy difference between the energy of an activated complex and the energy of its precursor. If the activated complex in the sublimation process is a cluster of loosely bound molecules of forthcoming products and its precursor is a strongly bound molecule then the Arrhenius equation for the volatilization of alkylammonium hexachlorostannates should be written in the form: $Z \exp[-E/(5RT)]$, since E pertains to five molecules of gaseous species. This conception is analogous to one assumed by Meshi and Searcy [85] for explaining the energetics of an activated complex in sublimation processes. On the other hand, it remains in contradiction with Schultz and Dekker's [71] theory of sublimation and further works of Chaiken et al. [72] and Kishore and Pai-Verneker [76]. Following the assumption made above all the values of E derived on the basis of eqn. (6) should be multiplied by 5 and then real physical meaning can be ascribed to them.

The above considerations present a reasonable, but certainly not unique, explanation for the existence of an energy barrier in the dissociative sublimation processes of complex molecules.

It is worthwhile to mention that the questions raised above regarding the form of the Arrhenius equation do not just concern the kinetics of sublimation of alkylammonium hexachlorostannates. Similar confusion always exists when a large molecule decomposes into several smaller fragments. One can notice, reviewing the literature concerning kinetics, that not much attention has been devoted to this problem in the past.

THERMOCHEMICAL CHARACTERISTICS

In the most recent work devoted to the thermal properties of primary *n*-alkylammonium chlorides we have shown that several important thermochemical characteristics can be derived on the basis of the knowledge of the enthalpy of sublimation of the salts [65]. The various relations between the thermochemical quantities for the compounds examined in this work are presented in Fig. 2.

All magnitudes shown in the thermochemical cycle refer to 298 K and 1 atm. The meanings of the other symbols are listed: ΔH_f represents the enthalpy of formation of a given substance; $U + 3RT$ is the lattice enthalpy; U denotes the lattice energy; and ΔH_s identifies the enthalpy of sublimation.

Enthalpy of sublimation at 298 K

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

$$\Delta H^0_{\mathrm{s},298} = \Delta H^0_\mathrm{s} + \Delta H^0_\sigma - \int_{298}^{T} \Delta C^0_\mathrm{p} \, \mathrm{d}T \qquad (7)$$

where ΔH^0_s represents the values for the enthalpy of sublimation evaluated by us (Table 4); term ΔH^0_σ arises from any polymorphic transitions which

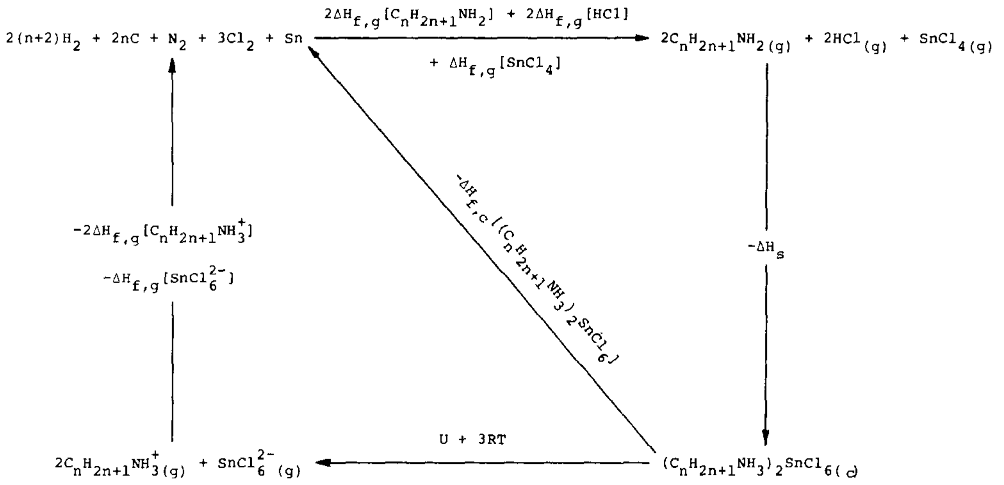


Fig. 2. The thermochemical cycle.

these compounds may undergo between 298 K and the beginning of the sublimation process; and the term $\int_{298}^{T} \Delta C_p^0 \, dT$ accounts for changes of enthalpy resulting from changes in heat capacity of the reactants.

Some of the compounds investigated undergo phase transitions in the temperature range of interest. Unfortunately, the pertinent data for ΔH_σ are not available. Therefore, we neglect this term assuming that it does not significantly influence the $\Delta H_{s,298}^0$ values. Some justification for this step can be found in the work of Matsuo et al. [64] who estimated the enthalpy of the phase transition for methylammonium hexachlorostannate to be below 2 kJ mol^{-1}.

The magnitude and sign of the heat capacity term is also difficult to assess in the absence of appropriate heat capacity data for the majority of reactants. For the first compound of the series the heat capacity term was estimated to be ca. -10 kJ mol^{-1}. This value was calculated within the temperature limits 298–550 K using available heat capacity data for NH_3 [88], HCl [88] and $SnCl_4$ [89]. In the absence of heat capacity data for $(NH_4)_2SnCl_6$ in the above mentioned temperature limits we assume that C_p^0 can be approximated by the equation: $213.1 + 0.173T$ (J mol^{-1} K^{-1}), which has been derived on the basis of heat capacity measurements in the temperature range 250–300 K [90]. For other compounds examined we assume the value of the heat capacity term to be the same as for $(NH_4)_2SnCl_6$. Two facts can justify such an assumption. Firstly, sublimation of primary *n*-alkylammonium hexachlorostannates proceeds in a temperature range similar to that for the sublimation of $(NH_4)_2SnCl_6$. Secondly, the expected changes of heat capacity caused by an increase in size of the alkyl group should be identical for salts and appropriate amines. Thus, the change in size of the alkyl group may not influence ΔC_p^0.

TABLE 6

Thermochemical data for $(C_nH_{2n+1}NH_3)_2SnCl_6$ at 298 K

n	ΔH_s^0 (kJ mol^{-1})	$\Delta H_{f,c}^0$ (kJ mol^{-1})		U^0 (kJ mol^{-1})		
		This work	From literature	From the thermochemical cycle	From the Kapustinskii–Yatsimirskii equation	From literature
0	465 [a]	−1213	−1281 [25] −1244 [31] −1237 [83]	1309	1421	1370 [4]
1	484	−1197		1235	1339	
2	467	−1228		1191	1337	
3	481	−1302		1195	1335	
4	506	−1386		1214	1339	
5	518	−1458		1224	1339	
6	491	−1491		1195	1346	
7	474	−1534		1177	1339	
8	516	−1635		1218	1348	

[a] Mean value from data No. 1, 4 and 7 (see Table 4).

Taking into account the above considerations we derived values of $\Delta H_{s,298}^0$ for all the compounds studied. They are listed in Table 6.

Enthalpy of formation of $(C_nH_{2n+1}NH_3)_2SnCl_6$

From the thermochemical cycle presented in Fig. 2 the following relationship results:

$$\begin{aligned}\Delta H_{f,c}^0&[(C_nH_{2n+1}NH_3)_2SnCl_6]\\&=2\Delta H_{f,g}^0[C_nH_{2n+1}NH_2]+2\Delta H_{f,g}^0[HCl]\\&+\Delta H_{f,g}^0[SnCl_4]-\Delta H_s^0\end{aligned}\tag{8}$$

Using values of $\Delta H_{f,g}^0[C_nH_{2n+1}NH_2]$ from our previous work (ref. 65, Table 7) together with the values of ΔH_s^0 evaluated in this work (Table 6) and taking $\Delta H_{f,g}^0[HCl] = -92.3$ kJ mol^{-1} [3,88] and $\Delta H_{f,g}^0[SnCl_4] = -472$ kJ mol^{-1} [83] we derived values of the standard enthalpy of formation of crystalline mono-*n*-alkylammonium hexachlorostannates. They are also listed in Table 6.

Crystal lattice energy

Another important characteristic which can be derived on the basis of the knowledge of ΔH_s^0 is the crystal lattice energy. The most convenient form for calculating of this magnitude is that presented by eqn. (9), viz.

$$U^0 = 2\Delta H^0_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3^+] + \Delta H^0_{\mathrm{f,g}}[\mathrm{SnCl}_6^{2-}]$$
$$-\Delta H^0_{\mathrm{f,c}}[(\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3)_2\mathrm{SnCl}_6] - 3RT \qquad (9)$$

The numerical values of $U^0[(\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3)_2\mathrm{SnCl}_6]$ were calculated using values of $\Delta H^\circ_{\mathrm{f,g}}[\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3^+]$ from our previous work (ref. 65, Table 8) and values of $\Delta H^0_{\mathrm{f,c}}[(\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3)_2\mathrm{SnCl}_6]$ from this work (Table 6). For $\Delta H^0_{\mathrm{f,g}}[\mathrm{SnCl}_6^{2-}]$ we took a value equal to -1156 kJ mol^{-1} [4]. The derived crystal lattice energies are listed in Table 6. The comparison of these U^0 values with the literature values is possible only in the case of the simplest representing this series. The value of U^0 derived by us is slightly lower than the literature value. Nonetheless, the agreement is quite good taking into account the totally different way in which these two characteristics have been derived.

To gain possible further insight into this problem we invoked an approximate method originally proposed by Kapustinskii [91] for evaluating the crystal lattice energies. In this work we applied the equation taken from the work of Yatsimirskii [92]:

$$U = 120.2\frac{\left(\sum n\right)Z_\mathrm{K}Z_\mathrm{A}}{r_\mathrm{K}+r_\mathrm{A}}\left[1 - \frac{0.0345}{r_\mathrm{K}+r_\mathrm{A}} + 0.087(r_\mathrm{K}+r_\mathrm{A})\right](\mathrm{kJ\ mol^{-1}}) \qquad (10)$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule; Z_K and Z_A represent 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 make any use of eqn. (10) the "thermochemical" radii of appropriate ions have to be known. Only for spherical ions can crystal ionic radii be substituted instead of "thermochemical" ionic radii. For non-spherical ions adequate "thermochemical" ionic radii have to be calculated on the basis of eqn. (10). Therefore, we derived values of r_K for appropriate $\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3^+$ ions using values of U^0 evaluated in our previous work for mono-n-alkylammonium chlorides [65] and assuming $r_{\mathrm{Cl}^-} = 0.172$ nm [93]. The following values for r_K have been obtained: 0.145, 0.179, 0.180, 0.181, 0.179, 0.179, 0.176, 0.179 and 0.175 for $n = 0$–8, respectively. Assuming, further, for $r_{\mathrm{SnCl}_6^{2-}}$ a value equal to 0.349 nm [93] we calculated crystal lattice energies for primary n-alkylammonium hexachlorostannates. These values are listed in Table 6.

Two important regularities can be noticed on the basis of the above considerations. Firstly, the values of the "thermochemical" radii for $\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{NH}_3^+$ ions are almost equal in the range of n between 1 and 8. Only for NH_4^+ is the "thermochemical" radius much lower. Secondly, the values of U derived on the basis of eqn. (10) generally show the same trends as those obtained from the thermochemical cycle. However, the former values are more than 100 kJ mol^{-1} higher than the latter ones. Despite the fact that one can consider the agreement between these two sets of values of U as quite good, we believe that the agreement could be improved if one assumes for $r_{SnCl_6^{2-}}$ a value higher than that given in ref. 93. To strengthen this suggestion we took pains to calculate the crystal lattice energies for ammonium, potassium, rubidium and caesium hexachlorostannates using available data for r_K [88,93] and taking for $r_{SnCl_6^{2-}}$ a value equal to 0.349 nm [93]. Also in this case much higher values of the crystal lattice energy, than those reported in the literature [4], were obtained. We do not intend to make any correction for $r_{SnCl_6^{2-}}$ at this moment. We would like only to mention that this factor presumably accounts mostly for the disagreement of the crystal lattice energy values derived by both methods applied. We would like to present a proposition regarding a new value for the "thermochemical" radius of the $SnCl_6^{2-}$ ion after gathering more evidence.

Final remarks

The technique applied in this work appears to be very useful not only for examination of the thermal properties of alkylammonium hexachlorostannates but also for evaluation of very important thermochemical characteristics for them.

The values of ΔH_s^0 derived in this work are slightly lower than those calculated on the basis of the standard enthalpy of formation of the reactants. This regularity seems to be very general. Applying dynamic methods one usually gets lower values for the enthalpy of reaction. Despite this small discrepancy, the results of this work strongly support the concept of the existence of kinetically independent fragments in the gas phase. If interactions between the gaseous products were strong, one could expect much lower values of ΔH_s^0.

Finally, it is immensely interesting that both the enthalpies of sublimation and the crystal lattice energies of the compounds studied change only insignificantly with increasing size of alkyl substituent. It would mean that the distances between charged centres in the crystal lattice remain principally unchanged, as lattice energy is affected predominantly by the coulombic interaction. It would also suggest that the alkyl chain is located in the crystal lattice in such a way that it does not significantly influence the distances between the charged centres. Of course, these statements require further confirmation, among others, by calculation of the crystal lattice energies. This problem is being considered in our laboratory.

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