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THERMAL FEATURES, THERMOCHEMISTRY AND KINETICS OF THE THERMAL DISSOCIATION OF HEXACHLOROSTANNATES OF AROMATIC MONO-AMINES

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ABSTRACT

Thermal properties of hexachlorostannates of several aromatic mono-amines have been examined by thermoanalytical methods (TG, DTG and DTA). Most of the compounds studied undergo complete volatilization upon heating, accompanied by a release of amines, HCl and $SnCl_4$ to the gaseous phase. The thermal dissociation of these derivatives is realized in essentially one step, in which up to 84% of the sample volatilizes. This is followed by a slow step, seen as a 'tail' in TG curves, in which the remaining part of the sample disappears. For some of the compounds, this simple thermal dissociation pattern is disturbed by the occurrence of side processes leading, among other outcomes, to the carbonization of organic fragments of molecules.

The thermodynamics and kinetics of the thermal dissociation process were studied using non-isothermal TG curves. Enthalpies of volatilization were evaluated using the van't Hoff equation. The enthalpies of formation and crystal lattice energies of crystalline hexachlorostannates were then evaluated using the derived values of the enthalpies of volatilization and taking other thermochemical characteristics from the literature. The crystal lattice energy problems were also examined within the framework of the Kapustinskii–Yatsimirskii formula. The kinetics of the thermal processes were also considered according to the Arrhenius approach. The Jacobs and Russell–Jones theory is invoked to explain qualitatively the diminution of the rate of volatilization at the end of the process.

INTRODUCTION

Numerous tetrahalides of the Main Group IV elements (MX_4) form, in acidic HX media, complex MX_6^{2-} ions. Whether or not such ions form depends on the dimensions of the central atom and the surrounding halide atoms [1]. However, the stability of MX_6^{2-} ions is determined by the oxido-reductive features of the central atom relative to those of the halide ligands [2,3]. According to the model of a close-packing of ligand atoms around the central atom, the dimensions of the constituents of the MX_6^{2-} ions must correspond such that repulsive forces between the ligands do not exceed attractive forces between M and X [1]. This model explains why

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CCl_6^{2-} ions do not exist. Among SiX_6^{2-} ions, only SiF_6^{2-} is known [1,4–6]. The formation of appropriate complex ions of Si with chlorine, bromine and iodine is hindered by the small size of the central atom as compared with the ligand atoms [1]. The homologous MX_6^{2-} ions of Ge, Sn and Pb can exist potentially, but, as mentioned above, their stability is affected by the oxido-reductive features of M and X. The redox potentials (all in V) of halides ($F_2/F^- = 2.87$, $Cl_2/Cl^- = 1.36$, $Br_2/Br^- = 1.07$, $I_2/I^- = 0.535$) [7] and Group IV elements ($Ge^{4+}/Ge^{2+} = -0.12$, $Sn^{4+}/Sn^{2+} = 0.15$, $Pb^{4+}/Pb^{2+} = 1.5$) [7,8] indicate that all MX_6^{2-} ions except PbX_6^{2-} ($X \equiv Cl$, Br or I) should be stable. The latter species show a tendency to undergo the intermolecular redox reaction leading to the formation of divalent lead derivatives and X_2 molecules. Thus, the corresponding salts are unstable, and sometimes cannot even be synthesized. The Ge^{4+}/Ge^{2+} potential indicates that the system is rather weakly reductive, which means that GeX_6^{2-} ions do not tend to undergo intermolecular redox reactions. The behaviour of SnX_6^{2-} ions is similar, although the Sn^{4+}/Sn^{2+} system shows weak oxidative features. Thus, $SnCl_6^{2-}$ is one of the most stable MX_6^{2-} ions, owing to the low Sn^{4+}/Sn^{2+} potential and highly favoured steric arrangement of the Sn and Cl constituents [1]. For this reason, the $SnCl_6^{2-}$ ion is often used as a model complex ion for investigative purposes. These distinctive features drew $SnCl_6^{2-}$ to our attention and provoked us to examine the thermal properties and thermochemistry of selected derivatives containing a wide variety of cations, including alkanaminium cations [2,3] and cations of mononitrogen organic bases [9]. The present work is a continuation of these studies, and examines the thermal behaviour of hexachlorostannates of aromatic mono-amines. Little is known about the compounds chosen for these investigations or their properties [10–14]. The study was undertaken in order to gather more information on the behaviour of salts composed of highly unsymmetrical cations, and on the nature of interactions between acids and nitrogen organic bases. Besides their purely scientific interest, such studies may also prove to be of some practical importance.

EXPERIMENTAL

The sources of amines used, methods for their purification, and analytical procedures for checking their purity were as described in an earlier work [15]. Other reagents used were of analytical grade. The hexachlorostannates of benzenamine (**1**), *N*-methyl-benzenamine (**2**), *N*,*N*-dimethyl-benzenamine (**3**), benzenemethanamine (**6**), *N*-methyl-benzenemethanamine (**7**) and *N*,*N*-dimethyl-benzenemethanamine (**8**) were synthesized by mixing aqueous solutions of hydrochlorides of appropriate amines with stoichiometric amounts of a solution of $SnCl_4 \cdot 5H_2O$ in dilute HCl (molar ratio, 2 : 1)

[3,9–12]. The crystals formed were filtered, carefully washed with 0.1 M HCl solution, and dried in a vacuum desiccator over P_2O_5. The hexachlorostannates of *N*-methyl-*N*-phenyl-benzenamine (**5**) and *N*-methyl-*N*-phenyl-benzenemethanamine (**9**) were prepared in a manner similar to that described above, mixing the components in a H_2O–CH_3OH medium. The hexachlorostannate of *N*-phenyl-benzenamine (**4**) was obtained by mixing stoichiometric amounts (molar ratio, 2 : 1) of concentrated solutions of amine and H_2SnCl_6 in CH_3OH and slowly evaporating the solvent. The resulting solid product was filtered and dried in a vacuum desiccator over P_2O_5. The compositions of the compounds were confirmed by elemental analysis (performed on a Carlo–Erba instrument, model 1106). An attempt was also made to synthesize hexachlorostannates of other aromatic amines, for which the appropriate hydrochlorides had been prepared previously [15]. Unfortunately, we did not succeed.

Dynamic thermal analyses were carried out using an OD-103 derivatograph (Monicon, Hungary) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen. The samples, of weight 100 mg, were placed on one platinum plate of the polyplate sample holder (see ref. 16, Appendix 1, No. 4). The heating rate was 4.65 ± 0.15 K min^{-1}, and the sensitivities of the DTG, DTA and TG galvanometers were 1/10, 1/1.5 and 100 mg, respectively. Thermogravimetric analyses in quasi isothermal–isobaric conditions [17] were performed on a Q-1500 derivatograph (Monicon). Samples of 100 mg were placed in a special platinum labyrinth crucible, and heated at a rate of ca. 3 K min^{-1}. The rate of mass loss was adjusted to be 2 mg min^{-1}. The temperatures T corresponding to appropriate values of the degree of volatilization α were determined from the thermogravimetric curves (see e.g. Fig. 1) according to a method described previously [18]. The range of α over which these data points were taken was chosen by examining 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.

TABLE 1

α vs. T dependence for the volatilization of benzenaminium hexachlorostannate (**A**), benzenemethanaminium hexachlorostannate (**B**) and *N*,*N*-dimethyl-benzenemethanaminium hexachlorostannate (**C**) (cf. Fig. 1)

	T (K) at $\alpha =$									
	0.08	0.16	0.24	0.32	0.40	0.48	0.56	0.64	0.72	0.80
A	466.3	478.0	486.3	492.0	496.7	501.3	505.3	508.7	511.7	516.0
B	519.3	535.7	543.7	549.0	556.3	559.7	565.3	568.7	572.0	577.0
C	505.7	518.3	530.3	537.3	542.7	547.3	551.7	555.7	559.3	563.7

RESULTS

The dynamic thermoanalytical curves obtained for two compounds chosen as examples are shown in Fig. 1. To enable further discussion we have also compiled (Table 2) characteristic parameters resulting from examination of the thermal analysis curves, together with data from the literature. The dynamic thermoanalytical measurements indicate that decomposition of most of the hexachlorostannates examined, i.e. compounds **1**, **2**, **4**, **5**, **6**, **7** and **8**, is accompanied by complete volatilization of the solid substance (Fig. 1). The TG curves for compounds **1**, **2**, **4**, **5** and **6** demonstrate that the process proceeds in two stages (see e.g. Fig. 1A). The first fast step, during which up to 84% of the sample volatilizes, is followed by a slow step (seen as a 'tail'), during which the remainder of the sample disappears. Similar effects have been observed upon thermal dissociation of numerous alkanaminium chlorides and hexachlorostannates [3,20], hydrochlorides and hexachlorostannates of mono-nitrogen aromatic bases [9,21], as well as hydrochlorides of aromatic amines [15]. Complementary studies have shown that the remainder which volatilizes in the second stage has the same composition as the original sample. The observed phenomenon is thus likely to be the result of a decrease in the rate of the process as a consequence of physical processes in a volatilized substance. This problem will be discussed later. It is worth mentioning that TG analyses for the latter compounds,

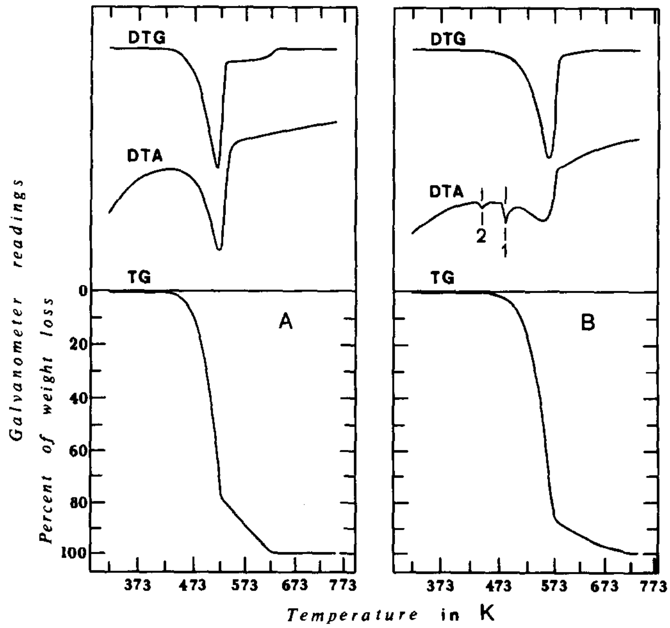

Fig. 1. Thermal analyses of hexachlorostannates of benzenamine (A) and *N*,*N*-dimethyl-benzenemethanamine (B) in dynamic conditions. 1 and 2 represent the melting and the solid phase transition, respectively.

performed in Q-conditions, also demonstrate total volatilization of samples upon heating (see, for example, Fig. 2A), despite the fact that the process takes place within a much higher temperature range. The dynamic thermoanalytical curves reveal that thermolysis of compounds **7** and **8** proceeds in a manner similar to that of the aforementioned derivatives to the far extent of the process. At the end of the volatilization, however, side reactions occur which alter the shape of the TG curve 'tail' so that it differs somewhat from that characteristic for the completion of the thermal processes for compounds **1**, **2**, **4**, **5** and **6** (see, for example, Fig. 1B). The occurrence of side reactions upon heating of compounds **7** and **8** has also been confirmed by Q-thermogravimetric measurements (see, for example, Fig. 2B). As the conditions of thermolysis by the Q-method differ markedly from those characteristic of dynamic measurements, the heating of both substances in Q-mode leads to the formation of large amounts of poorly volatile material. Compounds **3** and **9** exhibit an even more complex thermal decomposition pattern. Both dynamic thermoanalytical measurements and Q-thermogravimetric investigations reveal that advanced decomposition of these substances begins relatively early. Indeed, the smooth dynamic thermoanalytical curve shape typical for simple volatilization is observed only in the range of α not exceeding 0.65 for compound **3**, and not exceeding 0.4 for compound **9**. The composition and nature of the solid residues were not examined.

A comparison of melting point values from the literature and values determined using the standard capillary method with some peak temperatures in the DTA curves permitted identification of the thermal effects resulting from fusion. Effects originating from this process were only to be seen in the DTA curves for compounds **3**, **7** and **8**. Fusion processes for the other compounds studied were not monitored in our experiments. This most probably results from the fact that all the latter derivatives melt when the volatilization process is far advanced. The relatively weak thermal effects originating from fusion may thus be masked by much stronger thermal effects resulting from the volatilization process. The thermal effects which occurred before melting of compounds **7** and **8** were ascribed to solid phase transitions.

The temperatures of thermolysis, namely T_p (from DTG and DTA), $T_{0.01}$, $T_{0.08}$, $T_{0.72}$ and ΔT_α, are features characteristic of a given compound; nevertheless, some regularities are occasionally revealed. The most stable among the compounds studied are benzenemethanaminium hexachlorostannate and its *N*-methyl substituted derivatives in which the amino group is connected with the phenyl through a CH_2 unit. The thermal stability of hexachlorostannates of amines decreases when the amino group is attached directly to the aromatic ring (as e.g. for compounds **1**, **2** and **3**). A further decrease in thermal stability is observed for compounds **4** and **5**, containing two phenyl substituents at the nitrogen. It is also worth mentioning that the hexachlorostannate of *N*-methyl-*N*-phenyl-benzenemethanamine exhibits a

TABLE 2

Thermal characteristics of hexachlorostannates of aromatic mono-amines

Substance		Peak temperatures [a] (K)				Temperature [a] (K)					Parameters of the onset of the second stage	
No.	Amine	DTG	DTA			$T_{0.01}$ [c]		$T_{0.08}$	$T_{0.72}$	ΔT_α		
			T_σ	T_m [b]	T_p	A	B				α	T (K)
1	$PhNH_2$	509		566 (d) [11]	510	432	429	466.3	511.7	45.4	0.83	520
2	$PhNHCH_3$	509		524 (d) [10,12] 523–529 (d) *	512	434	432	469.7	517.7	48.0	0.76	520
3	$PhN(CH_3)_2$	502		439 (d) [12] 441–445 (d) * 454	503	423	421	460.0				
4	Ph_2NH	461			482	392	394	424.7	463.3	38.6	0.80	475
5	Ph_2NCH_3	465		480–483 (d) *	468	399	395	427.0	467.0	40.0	0.82	480
6	$PhCH_2NH_2$	570		561–569 (d) *	573	480	478	519.3	572.0	52.7	0.84	575
7	$PhCH_2NHCH_3$	563	379	453–459 * 468	560	468	466	512.3	569.7	57.4		
8	$PhCH_2N(CH_3)_2$	559	438	467–470 * 480	553	464	462	505.7	559.3	53.6		
9	$PhCH_2N(CH_3)Ph$	493		502–509 (d) *	491	438		467.3				

[a] Symbols taken from ref. 19. 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 degree of conversion is equal to α (i.e. $T_{0.08} = T_{\alpha=0.08}$); $\Delta T_\alpha = T_{0.72} - T_{0.08}$.

[b] * indicates T_m determined by the standard capillary method; (d) indicates melting with decomposition.

[c] Temperature of the onset of volatilization: A, derived from thermal analysis curves; B, determined from eqn. (2).

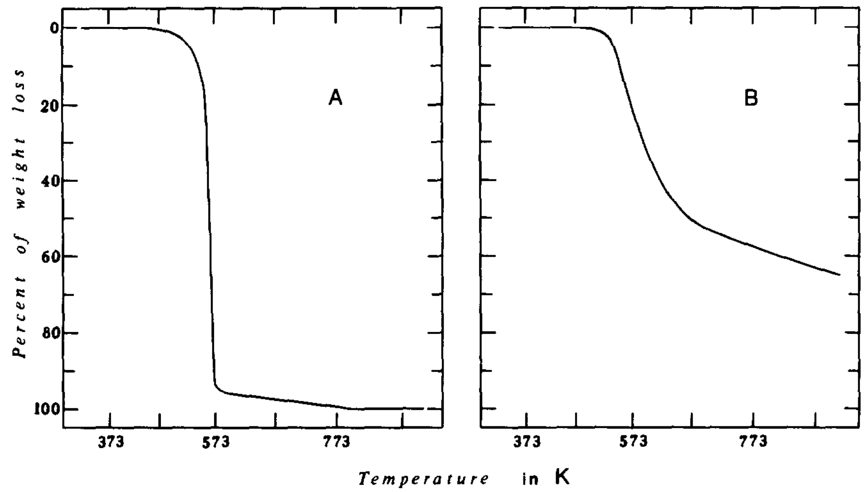

Fig. 2. Thermogravimetric analyses of hexachlorostannates of benzenamine (A) and *N,N*-dimethyl-benzenemethanamine (B) in quasi isobaric–isothermal conditions.

thermal stability similar to that of hexachlorostannates of phenyl-substituted amines, i.e. compounds **1**, **2** and **3**. Similar regularities have been observed for hydrochlorides of aromatic mono-amines [15], although the temperatures involved in the decomposition process of these derivatives are usually markedly lower than those characteristic of the corresponding hexachlorostannate salts.

DISCUSSION

Nature of the thermal process

Owing to the relatively strongly basic character of aromatic mono-amines, their derivatives, composed of protonated forms of parent molecules and anions of inorganic acids, should behave similarly to other salt-type derivatives of nitrogen bases. On this basis, it can be assumed that the mechanism for volatilization of hexachlorostannates of aromatic mono-amines exhibits the same features as the mechanisms we have discussed elsewhere for thermolysis of hexachlorostannates of alkanamines [2] and mono-nitrogen aromatic bases [9], as well as for volatilization of chloride salts of nitrogen bases [21,22]. Present knowledge of this problem indicates that the transfer of molecules from the condensed to the gaseous phase involves several stages. In the simple case (i.e. where side reactions do not occur), decomposition of the substrate is accompanied by the release of $SnCl_4$, HCl and amine molecules to the gaseous phase. The process can be summarized by the equation

$$(\mathrm{AmH})_2\mathrm{SnCl}_6(\mathrm{c}) \rightarrow 2\mathrm{Am}(\mathrm{g}) + 2\mathrm{HCl}(\mathrm{g}) + \mathrm{SnCl}_4(\mathrm{g}) \tag{1}$$

Such a summary of the volatilization process assumes the absence of any interactions between decomposition fragments in the gaseous phase. However, several recent theoretical calculations [23–25], as well as certain experimental findings [25–28] have indicated that amines and HCl can be associated, to some extent, in the gaseous phase. There is also a possibility of interactions between amine molecules and SnCl_4, since the latter compound exhibits features of a Lewis acid. Finally, weak interactions between amine molecules cannot be excluded [29–31]. The energy of all these interactions is relatively small in comparison with the enthalpy change accompanying the volatilization process. Therefore, it seems justifiable to assume that all evolved fragments behave as kinetically free molecules in the gaseous phase. Such an assumption forms a necessary framework for thermodynamic and kinetic considerations.

Thermodynamics of volatilization

Assuming that the thermal processes proceed at close to the equilibrium state and that interactions between products in the gaseous phase are negligible, the enthalpy of reaction (1) (ΔH_v) can be evaluated on the basis of the van't Hoff equation [2,3,9]. The equilibrium hypothesis implies that the only energy barrier existing for the process is a thermochemical one, i.e. ΔH_v. The thermoanalytical measurements were carried out in such a way as to limit side effects and bring the conditions under which the process occurred as close as possible to those of equilibrium. This issue has been discussed elsewhere [9,21]. Under the above conditions the experimental degree of conversion α is equal to P/P_0, where P is the equilibrium vapour pressure at a given T, and P_0 is the atmospheric pressure. The value of ΔH_v can thus be determined using the equation

$$\ln \alpha = -\frac{\Delta H_\mathrm{v}}{5R}\frac{1}{T} + \frac{\Delta H_\mathrm{v}}{5R}\frac{1}{T_\mathrm{v}} \tag{2}$$

where R is the gas constant; the factor 5 accounts for the fact that the dissociation of one $(\mathrm{AmH})_2\mathrm{SnCl}_6$ unit brings about five molecules of gaseous products; and T_v represents the volatilization temperature, i.e. the temperature at which P reaches P_0. The enthalpies of volatilization and T_v values derived in this way are shown in Table 3. The above procedure could not be applied in the case of *N*-methyl-*N*-phenyl-benzenemethanaminium hexachlorostannate, owing to the complex nature of its decomposition. The values of ΔH_v and T_v derived for this compound, on the basis of only four α

TABLE 3

Thermochemical and kinetic constants for the thermal dissociation of hexachlorostannates of aromatic mono-amines

Substance No. (Table 2)	Thermochemical constants [a]		Kinetic constants [b]				Range of α [c]
	ΔH_v (kJ mol^{-1})	T_v (K)	For the Polanyi–Wigner model: $g(1-\alpha)=\alpha$; (R1)		For the surface contracting area model: $g(1-\alpha)=1-(1-\alpha)^{1/2}$; (R2)		
			$E^\star$ (kJ mol^{-1})	Z (s^{-1})	$E^\star$ (kJ mol^{-1})	Z (s^{-1})	
1	476	518	456	2.2×10^5	508	1.6×10^6	0.08–0.72
2	478	522	457	2.1×10^5	510	1.6×10^6	0.08–0.72
3	449	513	429	8.8×10^4	472	4.1×10^5	0.08–0.64
4	472	469	461	3.2×10^6	505	1.9×10^7	0.08–0.72
5	454	474	436	6.4×10^5	484	4.7×10^6	0.08–0.72
6	520	580	497	1.3×10^5	554	7.8×10^5	0.08–0.72
7	467	577	445	1.6×10^4	496	8.7×10^4	0.08–0.72
8	474	568	452	2.9×10^4	503	1.7×10^5	0.08–0.72

[a] From eqn. (2). Values of ΔH_v and T_v were determined by applying a standard least-squares procedure. The linear correlation coefficient was always better than 0.996.

[b] From eqn. (3), rearranged to the form $\ln[g(1-\alpha)/T]$ vs. $1/T$. Values of $E^\star$ and Z were evaluated by a least-squares procedure. The correlation coefficient was always better than 0.995 in the case of the R1 model and better than 0.998 in the case of the R2 model.

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

vs. T data points, were uncertain and did not correspond to the rest of the derived thermochemical characteristics (Table 3).

Kinetics of thermal dissociation

The thermal dissociation of hexachlorostannates of nitrogen organic bases falls into the category of dissociative volatilization processes characterized by the fact that the typical physical process is accompanied by certain chemical changes in the system. One possible approach to the examination of kinetic phenomena in the systems studied is that based on the Arrhenius concept. The use of this method under dynamic conditions has been discussed elsewhere [32]. Following this approach, the general integral equation is of the form

$$g(1-\alpha) = Z\frac{T}{\Phi}\exp[-E^{\star}/5RT] \qquad (3)$$

where $g(1-\alpha)$ represents the kinetic model for the process (i.e. from the phenomenological point of view, the reaction pathway), Φ is the heating rate, and Z and $E^{\star}$ are the Arrhenius constants ($E^{\star}$ identifies the activation barrier for the process). The exponential term in eqn. (3) includes the factor 5. This modification of the classical Arrhenius equation results from an examination of the kinetics of volatilization of chloride and hexachlorostannate salts of various nitrogen organic bases [2,3,9,15,20,21]. It accounts for the fact that the transition state for the dissociative volatilization of the compounds studied is a loosely bound complex of two molecules of HCl, two molecules of amine and one molecule of $SnCl_4$. In such a case, the Arrhenius equation can be considered against five molecules of gaseous products released from the simplest structural unit of the hexachlorostannate molecule [9].

Using the experimental α vs. T dependences and eqn. (3), the values of Z and $E^{\star}$ were derived (Table 3) for two reaction models, namely the zero kinetic order model (R1) and the surface contracting area model (R2) [18]. These two models were chosen since they seem to correspond best to both the character of the process and the conditions under which the process takes place. Moreover, the R2 model has been considered in the past as a means of describing the kinetics of volatilization of some ammonium salts [33,34]. Examination of the kinetic constants listed in Table 3 reveals that the $E^{\star}$ values characterizing the R1 model are always slightly lower than the ΔH_v values, whereas the kinetic energy barriers corresponding to the R2 model always somewhat exceed the corresponding ΔH_v values. In most cases, the R2 model fits the experimental data points a little better. If this simple, purely phenomenological approach did indeed describe the kinetic phenomena accompanying dissociation of the compounds studied, it would mean that the process actually proceeds without an additional energy barrier over that resulting from the thermodynamical requirements (i.e. ΔH_v). This conclusion would, of course, strengthen the assumption made earlier as to the equilibrium character of the process. Nevertheless, the approach adopted presents only a purely formal description of the kinetic phenomena, without giving any true insight into the nature of the microscopic mechanism of the volatilization process.

The Arrhenius equation (eqn. (3)) fits the experimental TG curves for the first step of volatilization very well. However, the question arises as to how to explain the existence of the second stage in the process, seen as a 'tail' in the TG curves for compounds **1**, **2**, **4**, **5** and **6**. A semi-quantitative explanation of this effect is possible on the basis of the Jacobs and Russell-Jones theory for dissociative volatilization processes [33]. We have discussed this issue in several previous works [2,3,9,15,20,21]. Present knowledge of this problem seems to indicate that a decrease in the rate of mass loss at the end of the process begins when the dimensions of the drops or crystals become relatively small. However, such an effect should gradually influence the volatilization process and thus affect smoothly the TG curves, as implied by the features of the Jacobs and Russell-Jones equation [22,33]. The pattern of thermoanalytical curves for compounds **1**, **2**, **4**, **5** and **6** (see, for example, Fig. 1A) reveals that the occurrence of the second stage is accompanied by certain non-continuous processes. One of these processes could be cracking of a thin layer of the liquid substance covering the whole surface of the flat platinum crucible, and the formation of small drops. The creation of drops would cause an increase in the cohesive forces in a volatilized material and, consequently, a decrease in the rate of volatilization. This qualitative explanation can account for the occurrence of two stages upon volatilization of the compounds which melt before or during the process. However, a similar effect is observed if the substance undergoes sublimation exclusively, as in the case of benzenaminium hexachlorostannate. As the above discussion demonstrates, the nature of this phenomenon is very complex, and further studies are necessary before it can be properly understood.

Thermochemical characteristics

The main aim of thermoanalytical investigations is to obtain information about the thermal behaviour and thermochemistry of the systems studied. In several earlier works we have shown that a knowledge of the enthalpy of volatilization of salt-type derivatives of nitrogen organic bases enables the evaluation of two important characteristics, namely, enthalpies of formation and crystal lattice energies [2,3,9,15,20–22]. Various relations between the thermochemical quantities can be conveniently presented in the form of a thermochemical cycle which is typical for all hexachlorostannate salts of nitrogen organic bases [2,9]. The following relationships result from such a cycle [2,3,9]

$$\Delta H^{\ominus}_{\mathrm{f,c}}[(\mathrm{AmH})_2\mathrm{SnCl}_6] = 2\Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{HCl}] + 2\Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{Am}] + \Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{SnCl}_4] - \Delta H^{\ominus}_{\mathrm{v}}[(\mathrm{AmH})_2\mathrm{SnCl}_6] \quad (4)$$

$$\Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{AmH}^+] = \Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{Am}] + \Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{H}^+] - PA[\mathrm{Am}] \quad (5)$$

$$U^{\ominus}[(\mathrm{AmH})_2\mathrm{SnCl}_6] = 2\,\Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{AmH}^+] + \Delta H^{\ominus}_{\mathrm{f,g}}[\mathrm{SnCl}_6^{2-}] - \Delta H^{\ominus}_{\mathrm{f,c}}[(\mathrm{AmH})_2\mathrm{SnCl}_6] - 3RT \quad (6)$$

where $\Delta H_{\mathrm{f}}^{\ominus}$ is the enthalpy of formation of a given species, PA denotes the proton affinity of the amine, $U^{\ominus}$ is the lattice energy, and $\Delta H_{\mathrm{v}}^{\ominus}$ is the enthalpy of volatilization. All magnitudes in eqns. (4)–(6) refer to 298 K and 1 atm. pressure.

The enthalpies of volatilization shown in Table 3 do not refer to 298 K and were therefore modified using the equation

$$\Delta H_{\mathrm{v}}^{\ominus} = \Delta H_{\mathrm{v}} + \Delta H_{\mathrm{fn}}^{\ominus} + \Sigma\Delta H_{\sigma}^{\ominus} - \int_{298}^{T} \Delta C_p^{\ominus}\,\mathrm{d}T \quad (7)$$

where ΔH_{v} denotes the enthalpy of volatilization derived from eqn. (2) (Table 3), $\Delta H_{\mathrm{fn}}^{\ominus}$ 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 the fusion or volatilization process, and $\int_{298}^{T} \Delta C_p^{\ominus}\,\mathrm{d}T$ accounts for the change in enthalpy resulting from changes in the heat capacities of the reactants. The enthalpies of fusion of hexachlorostannates of *N*,*N*-dimethyl-benzenamine, *N*-methyl-benzenemethanamine and *N*,*N*-dimethyl-benzenemethanamine were estimated to be 22, 34 and 27 kJ mol^{-1}, respectively, by comparison of the area of DTA peaks resulting from melting with those corresponding to the volatilization process, assuming the latter areas to be proportional to the corresponding ΔH_{v} values listed in Table 3. For the remaining compounds the term $\Delta H_{\mathrm{fn}}^{\ominus}$ was neglected, since either they do not melt, or they melt and decompose simultaneously ($T_{\mathrm{m}} > T_{0.08}$). In the latter case, the process of fusion presumably does not affect the thermodynamics of volatilization. In the same way as described above, the enthalpy of phase transition for *N*,*N*-dimethyl-benzenemethanaminium hexachlorostannate was estimated to be 8 kJ mol^{-1}. For the enthalpy of phase transition for *N*-methyl-benzenemethanaminium hexachlorostannate the value of 4 kJ mol^{-1} was taken arbitrarily [3]. In the absence of heat capacity data for hexachlorostannates and their decomposition fragments we have assumed for the heat capacity term the value -10 kJ mol^{-1}. The justification for such an assumption has been presented elsewhere [2,3,9]. The corrected values of $\Delta H_{\mathrm{v}}^{\ominus}$ are listed in Table 4.

To evaluate the thermochemical quantities from eqns. (4)–(6) we used available values for the enthalpies of formation and proton affinities of

TABLE 4

Thermochemical characteristics for aromatic mono-amines, their cations and hexachlorostannates at 298 K [a]

Substance	Am		AmH$^+$		(AmH)$_2$SnCl$_6$			
	$\Delta H^{\ominus}_{f,g}$	PA [b]	$\Delta H^{\ominus}_{f,g}$	r_K [15]	$\Delta H^{\ominus}_v$	$\Delta H^{\ominus}_{f,c}$	$U^{\ominus}$ [c]	
							A	B
PhNH$_2$	87.1 [31,35]	889 [31,41,42]	734	0.165	486	−968	1273	1324
PhNHCH$_3$	90.4 [36]	922 [31,41]	705	0.177	488	−964	1211	1298
PhN(CH$_3$)$_2$	100.5 [31,35,37]	945 [31,41,42]	692	0.206	481	−937	1158	1240
Ph$_2$NH	219.2 [35,38]				482	−700		
Ph$_2$NCH$_3$					464			
PhCH$_2$NH$_2$	87.8 [35,39]	918 [31,43]	706	0.152	530	−1011	1260	1353
PhCH$_2$NHCH$_3$					515			
PhCH$_2$N(CH$_3$)$_2$	84 [31]	961 [31]	659	0.204	519	−1008	1163	1244

[a] ΔH, PA and U in kJ mol^{-1}; r_K in nm.

[b] Proton affinities (mean values) were taken from the references given in square brackets, and were corrected relative to the PA value for ammonia of 860 kJ mol^{-1} [40].

[c] A, values determined from the thermochemical cycle; B, values evaluated from the Kapustinskii–Yatsimirskii equation.

gaseous amines (Table 4). The values of $\Delta H_{f,g}^{\ominus}[\mathrm{HCl}]$, $\Delta H_{f,g}^{\ominus}[\mathrm{SnCl_4}]$, $\Delta H_{f,g}^{\ominus}[\mathrm{H^+}]$ and $\Delta H_{f,g}^{\ominus}[\mathrm{SnCl_6^{2-}}]$ were assumed to be −92.3 [7,44], −472 [44], 1536.2 [7,44] and −1156 [45] kJ mol^{-1}, respectively. The derived thermochemical characteristics are shown in Table 4.

To shed more light on the crystal lattice energy problem, we invoked an approximate method developed originally by Kapustinskii and Yatsimirskii [46,47]. According to these authors, the crystal lattice energy of ionic compounds can be expressed using the equation

$$U = 120.2\frac{(\Sigma n)Z_K Z_A}{r_K + r_A}\left[1 - \frac{0.0345}{r_K + r_A} + 0.087(r_K + r_A)\right] \quad (\mathrm{kJ\ mol^{-1}}) \tag{8}$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule, Z_K and Z_A denote the numerical values of the charges of cation and anion, respectively, and r_K and r_A are the 'thermochemical' ionic radii (in nm). Using values of r_K from our previous work [15] (Table 4) and assuming a value of 0.37 nm for $r_{\mathrm{SnCl_6^{2-}}}$ [3], we determined the values of U listed in the last column of Table 4.

Concluding remarks

Evaluation of all the thermochemical characteristics of the compounds studied was not possible owing to the lack of pertinent data regarding proton affinities and enthalpies of formation of amines. Nevertheless, some regularities and correlations with thermal features of the compounds as described above can be reported. The most stable among the compounds examined are the hexachlorostannates of amines in which the phenyl substituents are not attached directly to the amino group. Thus, hexachlorostannates of benzenemethanamine and its *N*-methyl-substituted derivatives have relatively high enthalpies of volatilization and enthalpies of formation (Table 4). These characteristics correspond well with the relatively high temperatures of thermal dissociation (Table 2) and volatilization (Table 3). The same characteristics for hexachlorostannates of benzenamine and its methyl-substituted derivatives reveal a lower thermal stability compared to that of benzenemethanamine derivatives. The fragmentary data for hexachlorostannates of amines in which more than one phenyl is attached to the amino group indicate that these derivatives exhibit the lowest thermal stability among the compounds examined in this work.

The thermal stability of the hexachlorostannates studied is determined on the one hand from the values of $\Delta H_{f,c}^{\ominus}$, and on the other hand from the energeticity of the reaction

$$(\mathrm{AmH})_2\mathrm{SnCl_6(c)} \rightarrow 2\mathrm{Am\cdot HCl(c)} + \mathrm{SnCl_4(g)} \tag{9}$$

Taking values of $\Delta H_{f,c}^{\ominus}[(\mathrm{AmH})_2\mathrm{SnCl_6}]$ from Table 4 and available values of $\Delta H_{f,c}^{\ominus}[\mathrm{Am\cdot HCl}]$ from previous work [15], and assuming the value given above for $\Delta H_{f,g}^{\ominus}[\mathrm{SnCl_4}]$, it can be shown that reaction (9) is endothermic by 166, 144, 175, 107 and 174 kJ mol^{-1} for Am = benzenamine, *N*-methyl-benzenamine, *N*,*N*-dimethyl-benzenamine, benzenemethanamine and *N*,*N*-dimethyl-benzenemethanamine, respectively. This means that formation of the hexachlorostannates is thermodynamically more favoured than formation of the corresponding hydrochlorides. This fully explains the higher thermal stability of the hexachlorostannate salts as compared with the hydrochlorides, and is manifested by the higher values of the enthalpies of formation and higher temperatures characterizing the volatilization of the former derivatives. It is therefore difficult to explain why we should have been unable to synthesize hexachlorostannates of several amines for which the corresponding hydrochlorides are known [15]. Most probably, this is due to the relatively low solubility of the hydrochlorides of these amines. This means that the solubility product cannot be reached if synthesis is carried out in dilute solution. On the other hand, upon slow evaporation of dilute solutions containing all components in stoichiometric amounts, the solubility product is exceeded for both chlorides and hexachlorostannates, such that both salts crystallize simultaneously.

The values of the crystal lattice energies differ from each other only insignificantly. They decrease slightly with increasing degree of substitution in the amino group. However, the values of U do not depend on the features of the *N*-substituents. Similar, somewhat unexpected regularities have been observed for hexachlorostannates of other nitrogen organic bases [2,3,9], as well as numerous chloride salts of nitrogen organic bases [15,20–22]. In order to shed more light on this matter, let us recall that the main contribution to the crystal lattice energy is brought about by electrostatic interactions between the charged centres. To account for this effect, information as to the location of atoms in the lattice and thus charge distribution is necessary. These data could be drawn from the crystallographic structures. Unfortunately, none of the crystal structures for the compounds studied are known. The established crystal structures for several alkanaminium hexachlorostannates [48,49] and hexachlorostannates of some nitrogen organic bases [50,51] reveal that the atoms which are believed to participate predominantly in electrostatic interactions form hydrogen bonds of the type, N–H · · · Cl–M, which are invariably trifurcated, bifurcated, or at least highly bent. Crystallographic data also demonstrate that the distances between Cl and H–N in the various structures are affected only insignificantly by substituents in the amino group. It can also be supposed that the charge distribution on these atoms is not influenced markedly by features of the *N*-substituents. That means that the part of the crystal lattice energy resulting from the Coulombic interactions should be similar for all hexachlorostannate salts of nitrogen organic bases. This qualitatively explains the trends to be observed in the values for crystal lattice energy derived in this and our previous works [2,3,9].

The crystal lattice energy problems may also be examined on the basis of the Kapustinskii–Yatsimirskii formula. The values of U obtained using previously determined ‘thermochemical’ radii for cations (from examination of U values for hydrochloride salts) are, however, as much as 100 kJ mol^{-1} higher than corresponding values derived from the thermochemical cycle. This means that ‘thermochemical’ radii are not additive quantities for this type of derivative. The observed discrepancies in the U values presumably result from differences in the nature of the hydrogen bonds formed in hexachlorostannate and chloride salts of nitrogen organic bases. In chloride salts the hydrogen bond $N-H \cdots Cl$ is linear [52–55], contrary to the case of the hexachlorostannate salts discussed above, where the hydrogen bond is bent. This means that the ‘thermochemical’ radii for the same cation admit different values in combination with Cl^- and $SnCl_6^{2-}$ anions. On the other hand, the linear hydrogen bond in chloride salts should be more effective than the bent hydrogen bond in hexachlorostannate salts of nitrogen organic bases. Crystal lattice energy should be a measure of this effect. Indeed, the U values predicted from the Kapustinskii–Yatsimirskii formula are higher, since they refer to the linear hydrogen bond while crystal lattice energies obtained from the thermochemical cycle actually correspond to the bent hydrogen bond.

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