

THERMAL ANALYSIS AND THERMOCHEMISTRY OF ALKALI METAL HEXACHLOROSTANNATES

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The thermal behaviour of alkali metal hexachlorostannates of general formula A_2SnCl_6 ($A = Li, Na, K, Cs, Rb$) has been studied by thermoanalytical methods (dynamic TG, DTG and DTA, and Q-TG). The compounds decompose upon heating with total ($A = Li, Na$) or partial ($A = K, Rb, Cs$) release of $SnCl_4$ molecules to the gaseous phase. The enthalpies of the decomposition process have been evaluated on the basis of the Van't Hoff equation and using dynamic TG curves. The thermochemistry of the compounds was thoroughly examined particularly, with regard to the enthalpies of formation and crystal lattice energies, as well as enthalpy changes characterizing the dissociation process. These data revealed that stability of the compounds markedly increase with an increase in the size of alkali metal cation.

Salts composed of complex hexachlorostannate(IV) anions and alkali metal cations have been known for a long time [1, 2]. Many of their properties have been studied in the past [2]. However, knowledge of the thermochemistry of these derivatives is still incomplete [3-9]. The present work is devoted to the latter problem. It is a continuation of our earlier studies on the thermochemistry and thermal properties of hexachlorostannate salts containing cations of various types [10, 11]. Alkali metal hexachlorostannates exhibit certain catalytic features, they can be used as substrates for the production of pure inorganic materials [9, 12], they also have some meaning in chemical analysis [3, 9], therefore, the studies undertaken are of considerable practical importance.

Experimental

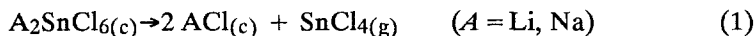
The compounds were synthesized by methods given in the literature [1, 2, 9]. Their identity was confirmed by Cl and Sn content determinations [9].

Thermal analyses in dynamic conditions were carried out on an OD-103 derivatograph placing the sample on one platinum plate of a polyplate

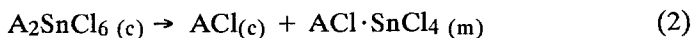
sample holder (conditions: mass of sample = 100 mg; heating rate = 2.5 or 5 deg·min⁻¹; α -Al₂O₃ served as a reference material; dynamic atmosphere of N₂). The quasi isothermal-isobaric measurements were performed on a Q-1500 derivatograph placing a sample weighing 100 mg in a special labyrinth platinum crucible (conditions: heating rate = 3 deg·min⁻¹; rate of mass loss = 2 mg·min⁻¹). Most of the compounds studied, were dried, prior to analyses, in a vacuum pistol, at temperatures below the onset of the thermal decomposition.

Results and discussion

The thermal analysis runs recorded in dynamic (D) and quasi isothermal-isobaric (Q) conditions for Li₂SnCl₆, chosen as an example, are shown in Fig. 1. The essential thermal and thermochemical characteristics for all the compounds studied are compiled in Table 1. Both dynamic and Q-thermogravimetric measurements reveal that Li₂SnCl₆ and Na₂SnCl₆ decompose upon heating in one stage. The weight loss corresponds exactly to the release of one SnCl₄ molecule from one hexachlorostannate unit. Thus, the thermal dissociation of these derivatives can be summarized by the equation:



Unfortunately, the remaining compounds studied exhibit a much more complex thermal decomposition pattern. This is revealed by the fact that decomposition of these derivatives never leads to the complete release of SnCl₄ in the first step. Moreover, the amounts of SnCl₄ evolved in that step varies from experiment to experiment for a given compound. A general tendency, however, exists namely the larger the size of the cation the lower the amount of SnCl₄ evolved in the first step. Following the work of Zalewicz [9] the thermal decomposition of potassium, rubidium and cesium hexachlorostannates proceeds in parallel by the reaction (1) shown above and the process which can be summarized by the equation:



The latter process is feasible if the crystals of the ACl·SnCl₄ units formed are more stable than those of the parent molecules. The shape of thermoanalytical curves indicates that thermochemical or perhaps kinetic

barriers for both reactions (1) and (2) are comparable (these processes can not be separated even in Q conditions). It is worth noting that only reaction (1) is accompanied by the loss of mass in the sample which implies that experimental thermogravimetric curves actually characterize this process exclusively.

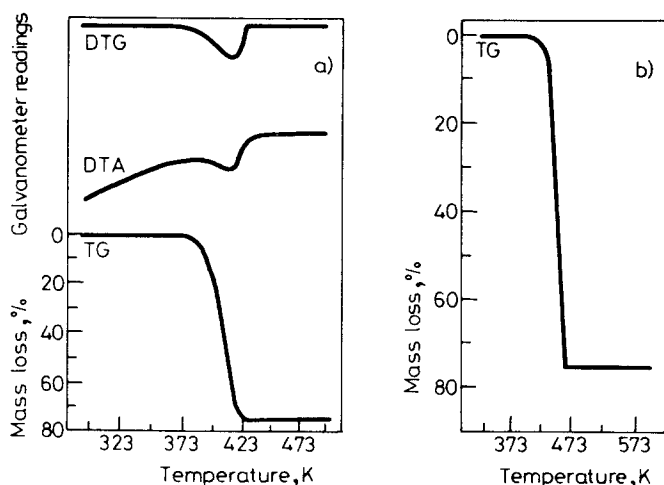


Fig. 1 Thermal curves of Li_2SnCl_6 in dynamic (a) and quasi isothermal-isobaric (b) conditions

For a simple process, such as that shown by Eq. (1), the enthalpy change (ΔH_d^0) can be evaluated on the basis of experimental α vs. T dependencies (α = extent of decomposition; T = temperature) and using Van't Hoff equation [13], namely:

$$\ln \alpha = - \frac{\Delta H_d^0}{R} \cdot \frac{1}{T} - \frac{\Delta H_d^0}{R} \cdot \frac{1}{T_v} \quad (3)$$

where R is the gas constant and T_v denotes decomposition temperature (i.e. temperature at which partial pressure of SnCl_4 attains atmospheric pressure). The use of Eq. (3) is justified if the process proceeds in conditions close to the equilibrium and if it does not require the overcoming of an additional energy barrier over that resulting from the thermochemical requirements (i.e. ΔH_d^0). The ΔH_d^0 values determined from Eq. (3), decomposition

Table 1 Thermal and thermochemical characteristics for alkali metal hexachlorostannates

Compound	Temperature, K			Thermochemical characteristics, $\text{kJ} \cdot \text{mol}^{-1}$ at 298 K					
	T_p		$T_\alpha = 0.01$	T_v		$\Delta H_f^{\circ,c}$ d	U°	ΔH_f°	
	DTA	DTG	a	b	c			b	c
Li ₂ SnCl ₆	416	415	376 (D)	367	419	-1384	1580	95	113
			415 (Q)						
Na ₂ SnCl ₆		457	410 (D)	406	462	-1444	1499	150	128
			445 (Q)						
K ₂ SnCl ₆	722	729	605 (D)	594	743	-1550	1416	205	113
			770 (Q)			-1479 [5]	1370 [5]		
Rb ₂ SnCl ₆		760	610 (D)	592	742 [4]	-1482 [6]	1363 [7]		
			870 (Q)			-1564	1381	221	97.6
						-1529 [18]	1551 [18]		136 [4]
Cs ₂ SnCl ₆		785	640 (D)	586	824	-1596	1348	238	77.8
			930 (D)				1361 [7]		188 [4]
							1558 [19]		
							1358 [7]		

^a Determined from dynamic (D) and quasi isothermal-isobaric (Q) thermoanalytical curves, ^b derived from Eqs (3), ^c from literature, ^d evaluated from Eq. (4) and (5)

temperatures and temperatures of the onset of decomposition ($T_{0.01}$) are listed in Table 1. Further information regarding the thermochemistry of the compounds studied can be drawn by considering the thermochemical cycles for both ACl and A_2SnCl_6 (see e.g. refs 10, 11). From these cycles the following two relationships can be derived:

$$\Delta H_{f,c}^{\circ}[\text{A}_2\text{SnCl}_6] = 2 \cdot \Delta H_{f,g}^{\circ}[\text{A}^+] + \Delta H_{f,g}^{\circ}[\text{SnCl}_6^{2-}] - U^{\circ}[\text{A}_2\text{SnCl}_6] - 3 \cdot R \cdot T \quad (4)$$

$$\Delta H_d^{\circ}[\text{A}_2\text{SnCl}_6] = 2 \cdot \Delta H_{f,c}^{\circ}[\text{ACl}] + \Delta H_{f,g}^{\circ}[\text{SnCl}_4] - \Delta H_{f,c}^{\circ}[\text{A}_2\text{SnCl}_6] \quad (5)$$

where ΔH_f° denotes the enthalpy of formation of a given species, ΔH_d° is the heat of decomposition and U° represents the crystal lattice energy. Values of U° for A_2SnCl_6 have been evaluated on the basis of the Kapustinskii-Yatsimirskii equation [14, 15] taking the value of the "thermochemical" radius (r) for SnCl_6^{2-} from the literature [11], and using values of $r(\text{A}^+)$ derived from the same formula and known crystal lattice energies of ACl and $r(\text{Cl}^-)$ [16, 17]. Using values of $U^{\circ}[\text{A}_2\text{SnCl}_6]$ thus derived and taking other data from literature [7, 11, 16], we evaluated the values of $\Delta H_{f,c}^{\circ}[\text{A}_2\text{SnCl}_6]$ and $\Delta H_d^{\circ}[\text{A}_2\text{SnCl}_6]$. All the latter characteristics, together with selected information from the literature are shown in Table 1. The enthalpies of the thermal dissociation derived from the Eq. (3) compare well with those determined from the thermochemical cycle only in the case of Li_2SnCl_6 and Na_2SnCl_6 .

Both thermal and thermochemical characteristics demonstrate that all the compounds studied are thermodynamically stable. The relatively low thermodynamic barriers for decomposition of Li_2SnCl_6 and Na_2SnCl_6 result in both compounds being highly hygroscopic and in some papers are reported as salts containing hydrated cations [1, 2]. The thermal stability of the compounds gradually increases with an increase in the size of the cation. This trend can be revealed by examination of both temperatures characterizing the decomposition process and thermodynamic quantities for the compounds $\Delta H_{f,c}^{\circ}$ and ΔH_d° .

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Zusammenfassung — Mittels thermoanalytischer Methoden (dynamische TG, DTG, DTA, Q-TG) wurde das thermische Verhalten von Alkalimetall-hexachlorostannaten der allgemeinen Formel A_2SnCl_6 ($A = Li, Na, K, Cs, Rb$) untersucht. Die Verbindungen zersetzen sich beim Erhitzen unter totaler ($A = Li, Na$) oder partieller ($A = K, Rb, Cs$) Freisetzung von $SnCl_4$ -Molekülen, die in die Gasphase übergehen. Die Enthalpien des Zersetzungsprozesses wurden auf der Grundlage der Van't Hoff'schen Gleichung unter Zuhilfenahme dynamischer TG-Kurven ermittelt. Die Thermochemie dieser Verbindungen wurde gründlich untersucht, in besonderem Hinblick auf Bildungsenthalpie und Kristallgitterenergie als auch auf Enthalpieänderungen, die den Dissoziationsprozess näher beschreiben. Die Untersuchungen zeigen, daß die Stabilität der Verbindungen mit anwachsender Alkalimetall-Kationengröße zunimmt.