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THERMOLYSIS OF ALKYLAMMONIUM HEXACHLOROSTANNATES

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ABSTRACT

Thermal properties of several alkylammonium hexachlorostannates were examined by TG, DTG and DTA with a derivatograph. All the compounds investigated undergo thermal decomposition which leads, in most cases, to the total volatilization of the salts. The thermodynamics and kinetics of the process were investigated based on the thermogravimetric traces. The enthalpy of formation and the crystal lattice energy of the salts were also estimated.

INTRODUCTION

The tetrachlorides of the main group IV elements (M) possess electron-acceptor properties which become stronger for the heavier elements. All the compounds of this group, with an exception of CCl_4, form octahedral MCl_6^{2-} ions. $PbCl_4$ has the most distinct electron-acceptor properties among MCl_4. Thermal behaviour of its complexes, including salts of H_2PbCl_6, have been studied thoroughly in this laboratory [1]. $PbCl_4$ is, however, thermodynamically unstable. It undergoes the intermolecular red-ox reaction which results from the higher Pb^{4+}/Pb^{2+} potential (+1.5 V) in comparison with that of Cl_2/Cl^- (+1.36 V). On the other hand, the Sn^{4+}/Sn^{2+} potential (+0.15 V) is relatively low, hence, $SnCl_4$ is thermodynamically more stable than $SnCl_2$. Therefore, for better understanding of the thermal properties of the complexes of MCl_4, it seems appropriate to extend the investigations on appropriate derivatives of $SnCl_4$. This work is devoted to the thermolysis of some alkylammonium salts of hexachlorostannic acid.

MEASURING METHODS

Alkylammonium hexachlorostannates were prepared by treating the solution of $SnCl_4$ in aqueous HCl (1:1) with appropriate cation chloride salts dissolved in hydrochloric acid [2]. The resulting white precipitates were filtered and dried in a vacuum

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desiccator over KOH and P_2O_5. The purity of the compounds was checked by elementary analysis.

The thermal analyses were carried out on an OD-103 derivatograph (Monicon).

RESULTS AND DISCUSSION

Thermal decomposition of some simple compounds of the series $\left[(n\text{-}C_pH_{2p+1})_MNH_{4-M}\right]_2SnCl_6$, where p=0-8 and M=1-4, results in the formation of gaseous $SnCl_4$, appropriate amines and HCl or alkyl chlorides. The latter compounds are formed during the dissociation of quaternary salts. With the increase of M the thermolysis process can appear more complex. This is revealed in the formation of a solid residue in the sample holder. The temperatures of the onset of the decomposition of hexachlorostannates are much higher than those of appropriate hydrochlorides [3] and hexachloroplumbates [1]. This fact could account for the complex course of thermolysis of some of the compounds as well as for the formation of solid products. In higher temperatures secondary processes such as the desctruction of organic fragments and oxidation with participation of the gas phase may become more pronounced.

The thermal analysis runs, shown in Fig. 1, are characteristic for all the types of the compounds investigated. Examining the thermal analysis data one notices that the dissociation of some of the compounds is preceded by phase transitions. Thermal analysis curves indicate also that the decomposition of quaternary hexachlorostannates proceeds generally in one stage, whereas volatilization of remaining salts investigated is accomplished in two distinct steps clearly seen on TG curves. Similar phenomenon has been observed earlier during the study of the dissociation process of appropriate chloride salts.

In the case of a simple decomposition pathway, the process can be expressed by the equation,

$$\left[(n\text{-}C_pH_{2p+1})_MNH_{4-M}\right]_2SnCl_{6\,(c)} \longrightarrow SnCl_{4\,(g)} + 2\left(n\text{-}C_pH_{2p+1}\right)_{M-a}NH_{3-M+a\,(g)} + 2(1-a)HCl_{(g)} + 2a\left(n\text{-}C_pH_{2p+1}\right)Cl_{(g)} \qquad (1)$$

where a=1 for quaternary salts and a=0 for other salts.

In the case of the compounds showing simple course of the thermal dissociation, the experimental TG traces can serve for the examination of kinetics and thermodynamics of the process.

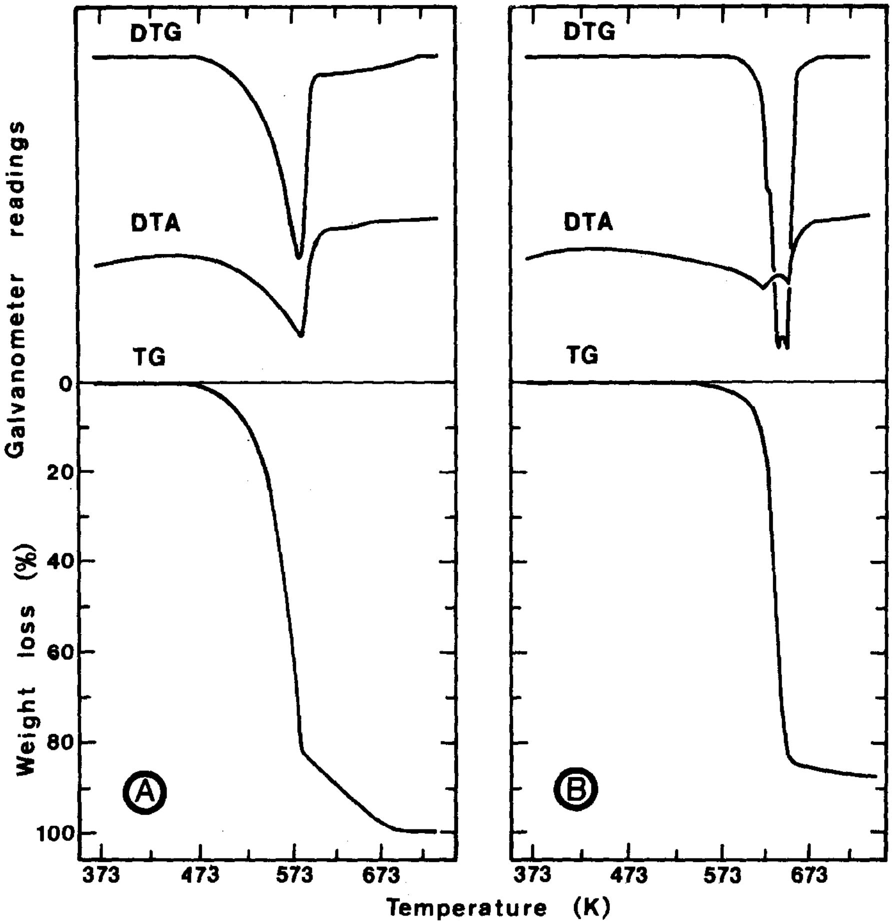

Figure 1. Thermal analyses of dimethylammonium hexachlorostannate (A) and tetra-n-butylammonium hexachlorostannate (B). Mass of samples = 100 mg; sample holder, one platinum plate [4] (Appendix 1, No. 4); reference material, α-Al_2O_3; heating rate = 5 K/min; galvanometer sensitivities: DTG = 1/10, DTA = 1/3 and TG = 100 mg; dynamic atmosphere of N_2.

The former problem has been studied adopting the Jacobs and Russell-Jones approach [5]. It was found that the kinetics of the first step of volatilization of the salts, with an exception of quaternary salts, is satisfactorily described by the equation [3],

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

where X_1, X_2 and E are the constants, Φ denotes the heating rate and α represents the degree of conversion at temperature T. The kinetic constants were derived using the least squares procedure [3].

The adopted description of kinetics allows to explain the presence of two stages in the process of thermal volatilization of primary, secondary and tertiary salts. This phenomenon results from the gradual decrease of the rate of reaction with a contraction of volume of grains of a solid phase.

Much more important are, however, thermochemical characteristics which are not available for the majority of alkylammonium hexachlorostannates. The enthalpy of the thermal decomposition (ΔH_d) were evaluated on the basis of the Van't Hoff equation. Then the enthalpy of formation($\Delta H_{f,c}$) and the energy of the crystal lattice (U) of the salts were derived according to Hess's law [3]. The required ancillary data have been taken from the literature.

Plotting the derived values of the thermochemical parameters for the primary n-alkylammonium salts versus the length of the aliphatic chain of amine one notices two important regularities. The values of $\Delta H_{f,c}$ gradually increase with an increase of p, whereas the values of ΔH_d and U remain practically constant. Whereas the former dependency is not surprising, the latter two require some comment. The almost constant values of U may suggest that distances between charged centers in the lattice remain pactically unchanged despite the length of an alkyl substituent. This means that alkyl chain is located inside the crystal lattice in such a way that it does not disturb the crystal structure. Of course, this statement requires further confirmations; among others by the theoretical calculations of the crystal lattice energy. The latter problem is being studied in our laboratory.

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