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THERMAL DECOMPOSITION OF ALKYLAMMONIUM HEXACHLOROPLUMBATES

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ABSTRACT

Thermolysis of several simple alkylammonium hexachloroplumbates was studied by TG, DTG and DTA with a derivatograph. The initial stage of the thermal decomposition of all the compounds investigated is the liberation of gaseous chlorine. This step is followed by the volatilization of appropriate amine hydrochlorides or decomposition of quaternary salts. The amounts of chlorine evolved were sometimes lower than stoichiometric as some of it was consumed in secondary processes. For the compounds showing well separate decomposition steps the thermodynamics and kinetics of the first stege were analyzed. Considerations regarding the structure of crystalline alkylammonium hexachloroplumbates, their enthalpies of formation and crystal lattice energies were also carried out.

INTRODUCTION

Solid derivatives of hexachloroplumbic acid may serve as the interesting model compounds for investigation of properties of hexachlorometallates of the main group IV elements owing to the unique behaviour of the central atom. Therefore, we undertook investigations regarding thermal properties of various salts of H_2PbCl_6 [1] and this work is a continuation of the cycle. It concerns thermolysis of simple alkylammonium hexachloroplumbates other than mono-alkyl. Thermal properties of the latter compounds have been the subject of our latest work in this cycle [1]. Extending the investigations we hoped to gather more information regarding thermodynamics and kinetics of thermolysis of this group of compounds and also to reveal correlations between the thermal properties and the structure of the alkyl substituent.

MEASURING METHODS

Alkylammonium hexachloroplumbates were prepared by the methods described previously [2]. Based on the Pb(IV) content (determined iodometrically), we found that all the compounds examined were more than 96% pure.

The thermal analyses were performed on an OD-103 derivatograph (Monicon). The isothermal experiments were carried out by the procedure described previously [2].

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RESULTS AND DISCUSSION

Alkylammonium hexachloroplumbates undergo decomposition upon heating to 700 K. Thermal decomposition of two compounds from this group, taken as an example, is shown in Fig. 1. Both compounds chosen show fairly simple decomposition pattern. The first stage corresponds to the release of one molecule of Cl_2 from one molecule of hexachloroplumbate and can be expressed by the equation,

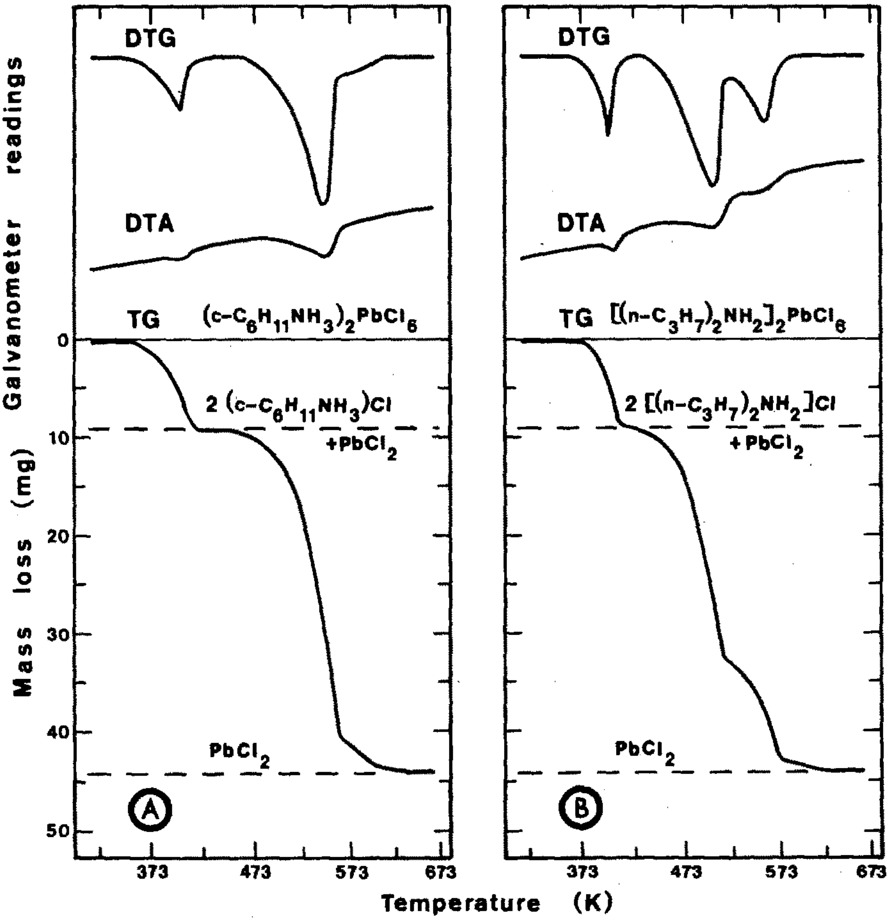

Figure 1. Thermal analyses of cycloheksylammonium hexachloroplumbate (A) and di-n-propylammonium hexachloroplumbate (B). Mass of samples = 80 mg; sample holder, one platinum plate [3] (Appendix 1, No. 4); reference material α-Al_2O_3; heating rate = 5 K/min; galvanometer sensitivities: DTG = 1/10, DTA = 1/5 and TG = 50 mg; dynamic atmosphere of N_2.

$$(R_nNH_{4-n})_2PbCl_{6(c)} \longrightarrow Cl_{2(g)} + \left[PbCl_2 + 2(R_nNH_{4-n})Cl\right]_{(s)} \qquad (1)$$

where R=alkyl.

Whereas the second step corresponds to the volatilization of two molecules of alkylammonium chloride from the mixture of solid products formed in stage I,

$$\left[PbCl_2+2(R_nNH_{4-n})Cl\right]_{(s)} \longrightarrow PbCl_{2(c)} + 2\,R_{n-a}NH_{3-n+a(g)} + 2(1-a)HCl_{(g)} + 2a\ RCl_{(g)} \qquad (2)$$

where a=1 for quaternary salts and a=0 for other salts. Reaction (2) proceeds smoothly, in one step (Fig. 1A), when the solid products of step I form the mixture of $PbCl_2$ and appropriate alkylammonium chloride. The process can exhibit, however, more complex nature if the solid products of step I interract during the heating forming additionally new solid phases. This is seen in the thermal analysis run of di-n-propylammonium hexachloroplumbate (Fig. 1B).

In the case of compounds showing well separate reaction stages usually stoichiometric amounts of chlorine are liberated to the gas phase in the first step. For the majority of the compounds investigated, however, both reaction stages overlap. Then the amounts of chlorine evolved are always lower than stoichiometric. Moreover, if isothermal experiments were carried out in the temperature limits corresponding to the second stage, the amounts of Cl_2 released were always lower than stoichiometric. The foregoing facts lead to the conclusion that chlorination processes presumably occur in the gas phase [1].

For the compounds showing well separate decomposition stages the thermodynamics and kinetics of the first step were analyzed. The enthalpy of the process (ΔH_d) was estimated according to the approximate method of Stepin et al. [4]. The values of ΔH_d evaluated for some of the compounds are shown in Table 1. They are in the same order of magnitude that are the values of ΔH_d previously derived for mono-n-alkylammonium hexachloroplumbates [1].

The energies of the crystal lattice of the salts were evaluated using the semi-empirical Kapustinskii-Yatsimirskii method [5]. Then the enthalpy of the thermal decomposition were estimated on the basis of the thermochemical cycle [6]. These remain in good agreement with the experimental values.

The kinetics of the thermal decomposition was analyzed based on the Coats and Redfern's approach [7] (method I) and method proposed previously by the authors [8] (method II). Substitution of various $g(1-\alpha)$ functions [6] to the appropriate form of the integral equations and application of various statistical methods [1] allows one to reveal the most adequate mechanism of the thermal process. In most cases the most favourable values of the statistical functions were obtained in the case of F1 mechanism. This might indicate that the loss of one molecule of Cl_2 from the molecule of hexachloroplumbate is controlled by a random nucleation of one nucleus on each particle. The values of the apparent activation energy for some of the compounds investigated are shown in Table 1.

Examination of the kinetics of the thermal decomposition of alkylammonium hexachloroplumbates again proved that the proposed by the authors equation, i.e.,

$$g(1-\alpha) = \frac{T}{\Phi} Z e^{-E/RT} \qquad (3)$$

where α is the degree of conversion at temperature T, Φ denotes the heating rate, R represents the gas constant, and E and Z are the constants, generally fits the experimental data better than other equations which are widely proposed in the literature.

Table 1. Thermochemical and kinetic parameters for some alkylammonium hexachloroplumbates

Compound (amine)	ΔH_d (kJ/mole)	Activation energy, E in kJ/mole for $g(1-\alpha)=-\ln(1-\alpha)$	
		method I	method II
cycloheksylamine	80.8	111	114
di-n-propylamine	94.7	121	125
piperidine	72.4	90.8	94.3

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