Thermochimica Acta, 66 (1983) 197–218
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL REACTIONS OF LEAD(IV) CHLORIDE COMPLEXES IN THE SOLID STATE. PART V. THERMOLYSIS OF MONO-*n*-ALKYLAMMONIUM HEXACHLOROPLUMBATES

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(Received 18 January 1983)

ABSTRACT

Ammonium and mono-*n*-alkylammonium hexachloroplumbates of general formula $(C_nH_{2n+1}NH_3)_2PbCl_6$, with $n = 0$–8, undergo thermal decomposition on heating to 650 K. The thermal processes were studied by differential thermal analysis and thermogravimetry with a derivatograph. Isothermal experiments were performed in an apparatus permitting a quantitative determination of amounts of evolved chlorine. For most compounds ($n > 2$) thermal processes proceed in two steps:

(I) liberation of chlorine

$$(C_nH_{2n+1}NH_3)_2PbCl_{6(s)} \rightarrow PbCl_{2(s)} + 2(C_nH_{2n+1}NH_3)Cl_{(s)} + Cl_{2(g)}$$

(II) thermal processes which occur on heating the solid products of step (I)

$$PbCl_{2(s)} + 2(C_nH_{2n+1}NH_3)Cl_{(s)} \rightarrow PbCl_{2(s)} + 2\ C_nH_{2n+1}NH_{2(g)} + 2\ HCl_{(g)}$$

The experimental TG and DTG curves were used to examine the thermodynamics and kinetics of the first decomposition step. In the kinetic treatment of the data, sixteen $f(\alpha)$ and corresponding $g(\alpha)$ functions which describe the primary mechanism of thermal decomposition of solid substances, i.e. nucleation, growth of nuclei, phase boundary reactions and diffusion processes, were applied in the least-squares error analysis. Seven of the most adequate forms of kinetic equations, five of them based on integral kinetic equations and two of them based on differential kinetic equations, were used to evaluate kinetic constants. This approach also gave us an opportunity to compare different forms of mathematical equations used in non-isothermal kinetics.

INTRODUCTION

Solid derivatives of hexachloroplumbic acid form the large group of fairly well-known compounds [1]. On the one hand this group holds compounds having properties of typical inorganic salts, as for example alkali metal hexachloroplumbates [2]. On the other hand to this group belong derivatives which are adducts rather than salt-like compounds, for instance compounds formed between H_2PbCl_6 and fairly weak *n*-electron donors like amides [3,4] or ethers [5]. Alkylammonium hexachloroplumbates are the largest group of

0040-6031/83/$03.00

solid derivatives of hexachloroplumbic acid which have been described and they also occupy an intermediate position among them. Therefore, knowledge of their thermal properties plays an important role in understanding the thermochemistry of solid derivatives of lead(IV) chloride.

Although alkylamines are considered as typical organic compounds they form salt-like derivatives with protonic acids. They are also strong electron donors and can form adducts with Lewis acids. Properties of alkylamines depend significantly on the structure of the alkyl substituent. Hence, one may also expect changes in thermal reactivity of alkylammonium salts with changes in the structure of the alkyl group.

In a continuation of our studies on the thermal reactions of lead tetrachloride derivatives in the solid state [2,4,6,7], we have extended our investigations on alkylammonium hexachloroplumbates. In a previous report, thermolysis of ammonium and methyl-substituted ammonium hexachloroplumbates has been described [7]. In this work thermal properties of mono-*n*-alkylammonium hexachloroplumbates were examined.

EXPERIMENTAL

Chlorine (P.O.Ch., Poland), ammonium chloride (P.O.Ch.), methylamine (B.D.H.), ethylamine (Fluka AG, Buchs SG), *n*-propylamine (UCB, Belgium), *n*-butylamine (Loba, Austria), *n*-amylamine (B.D.H.), *n*-hexylamine (Fluka AG, Buchs SG), *n*-heptylamine (Koch-Light Lab.) and *n*-octylamine (Koch-Light Lab.) were all obtained as pure grade and used as received. Other reagents of analytical grade have been used throughout.

Hexachloroplumbic acid and its ammonium and alkylammonium salts were prepared by the methods described previously [1,6,8]. The compounds were analysed for Pb(II) and Pb(IV). The results showed that all synthesized derivatives, with the exception of *n*-octylammonium hexachloroplumbate, were more than 96% pure. $[CH_3(CH_2)_7NH_3]_2PbCl_6$ could be prepared only of purity not better than 90%.

The thermal analyses were carried out on an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen. The sample was placed on a platinum plate (see ref. 9, Fig. 3e). Other operating conditions were: mass of sample = 80 mg, heating rate = 4.8 [$\pm$0.2] K min^{-1}, sensitivities of DTG, DTA and TG galvanometers = 1/10, 1/5 and 50 mg, respectively. Since the size of the particles may influence thermogravimetric measurements [10], analyzed compounds were ground in an agate mortar and all particles passing through a standard mesh (150 μm) were used for analyses.

The isothermal experiments were carried out by the procedure described previously [6]. The analytical methods used have been given earlier [6].

MATHEMATICAL TREATMENT OF THE THERMAL ANALYSIS DATA

The kinetic and thermodynamic constants of thermolysis were evaluated from parameters determined from the thermal analysis curves [2].

For each experimental run, nine values of degree of conversion (α) were chosen on the TG curves (see Table 1) and then corresponding values of temperatures (T) and the rates of weight loss ($\mathrm{d}\alpha/\mathrm{d}t$) were read from the thermogram. For each compound thermal analyses were performed at least three times and the appropriate mean T and $\mathrm{d}\alpha/\mathrm{d}t$ values were taken in further calculations. An example of the set of experimental data points in the case of thermal decomposition (step I) of *n*-hexylammonium hexachloroplumbate is given in Table 1. The calibration constants (k, see Fig. 1 in ref. 2) were estimated from the slope of TG curves at $\alpha = 0.5$.

Enthalpy of the thermal reactions

The enthalpies of thermal reactions were evaluated using an approximate method proposed by Stepin et al. [11]. Based on previous considerations [2] the enthalpies of dissociation (ΔH_d^0) of alkylammonium hexachloroplumbates can be evaluated from the equation

$$\ln \alpha = -\frac{\Delta H_\mathrm{d}^0}{RT} + \text{const.} \tag{1}$$

Kinetic parameters

The functional dependence of the degree of conversion on all parameters determining the kinetics of a given process is considered in the description of reaction kinetics in the solid state contained in ref. 12. Till now an approach has been adopted which distinguished temperature among the parameters influencing α [13]. Then, reaction kinetics under linear temperature increase conditions can be described by the well-known forms of differential and integral equations, eqns. (2) and (3), respectively.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \mathrm{f}(\alpha) Z \exp\left(-\frac{E}{RT}\right) \tag{2}$$

$$\mathrm{g}(\alpha) = \frac{Z}{\Phi}\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{3}$$

where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of reaction, Z is a constant, Φ is the linear heating rate and E is the apparent activation energy. The integral in eqn. (3) can be expressed in the form of an incomplete gamma function using the substitution $x = E/RT$ [14]

$$\int_0^T \exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \frac{E}{R}\int_x^\infty \mathrm{e}^{-x}x^{-2}\mathrm{d}x = \frac{E}{R}\mathrm{p}(x) \tag{4}$$

This integral cannot be resolved exactly and for calculations some approximate formulae are proposed [14]. The simplest of them is $p(x) \cong e^{-x}x^{-2}$ [eqn. (8) in ref. 14]. With this approximation, eqn. (3) can be expressed in the form proposed by Coats and Redfern [15].

$$\frac{g(\alpha)}{T^2} = \frac{ZR}{\Phi E} \exp\left(-\frac{E}{RT}\right) \tag{5}$$

As has been shown earlier, the use of eqn. (3) in the description of reaction kinetics causes some difficulties. To avoid these difficulties we found recently that relationships other than those presented by eqns. (2) and (3) can be used for these purposes [13]. They are given in eqns. (6) and (7) in the form of differential and integral equations, respectively.

$$\frac{d\alpha}{dt} = f(\alpha) Z\left(1 + \frac{E}{RT}\right) \exp\left(-\frac{E}{RT}\right) \tag{6}$$

$$g(\alpha) = T\frac{Z}{\Phi} \exp\left(-\frac{E}{RT}\right) \tag{7}$$

Equations (6) and (7) were derived with the assumption that under dynamic conditions the degree of conversion is a function of both temperature and time.

To evaluate kinetic constants from the foregoing kinetic equations, we applied statistical methods based on the least-squares error analysis. Thus, eqns. (5) and (7) can be rearranged to the more convenient logarithmic forms, respectively

Method A

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{ZR}{\Phi E} - \frac{E}{RT} \tag{8}$$

Method B

$$\ln\frac{g(\alpha)}{T} = \ln\frac{Z}{\Phi} - \frac{E}{RT} \tag{9}$$

which are suitable for use in applying linearization procedures [13]. From these relationships E and Z values can be evaluated. Also, the correlation coefficient may be considered as an indicator permitting the choice of the most adequate function $g(\alpha)$.

This very convenient approach cannot be applied, however, in each case, since many equations used in reaction kinetics cannot be reduced to the linear forms. Therefore, it is necessary to apply other statistical methods. In a previous work [13] Blazejowski proposed the rearrangement of any kinetic equation in such a way that Z is placed on the left-hand side and all variables and other parameters on the right-hand side. Thus from eqns. (2)–(7) we obtain

Method C based on eqn. (5)

$$Z=\frac{\Phi E}{RT^2}\frac{g(\alpha)}{\exp(-E/RT)} \tag{10}$$

Method D based on eqns. (3) and (4)

$$Z=\frac{\Phi R}{E}\frac{g(\alpha)}{p(x)} \tag{11}$$

Method E based on eqn. (7)

$$Z=\frac{\Phi}{T}\frac{g(\alpha)}{\exp(-E/RT)} \tag{12}$$

Method F based on eqn. (2)

$$Z=\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\frac{1}{\exp(-E/RT)} \tag{13}$$

Method G based on eqn. (6)

$$Z=\frac{\mathrm{d}\alpha/\mathrm{d}t}{f(\alpha)}\frac{1}{(1+E/RT)\exp(-E/RT)} \tag{14}$$

Equations (10)–(14) together with the statistical function

$$\delta=\frac{\sqrt{\frac{1}{N}\sum_{i=1}^{N}(\Delta_i-\bar{\Delta})^2}}{\bar{\Delta}} \tag{15}$$

where $\Delta_i = Z_i$ for any experimental data points, α_i, T_i and $\mathrm{d}\alpha_i/\mathrm{d}t_i$; $\bar{\Delta} = \frac{1}{N}\sum_{i=1}^{N}\Delta_i$; and N = number of experimental points, may be used in the search for an adequate reaction mechanism, as well as the values of kinetic constants. The criteria for applying this approach in the trial-and-error procedure have been established in our previous work [13].

In eqns. (2)–(14) the function $g(\alpha)$ and its differential form $f(\alpha)$ represents the hypothetical model of the reaction mechanism. In the present work we applied sixteen functions, $g(\alpha)$ or $f(\alpha)$, describing most of the processes controlling the kinetics of thermal decomposition of solid substances, i.e. nucleation, growth of nuclei, phase boundary reactions and diffusion processes. They were listed elsewhere (Table 1 in ref. 2).

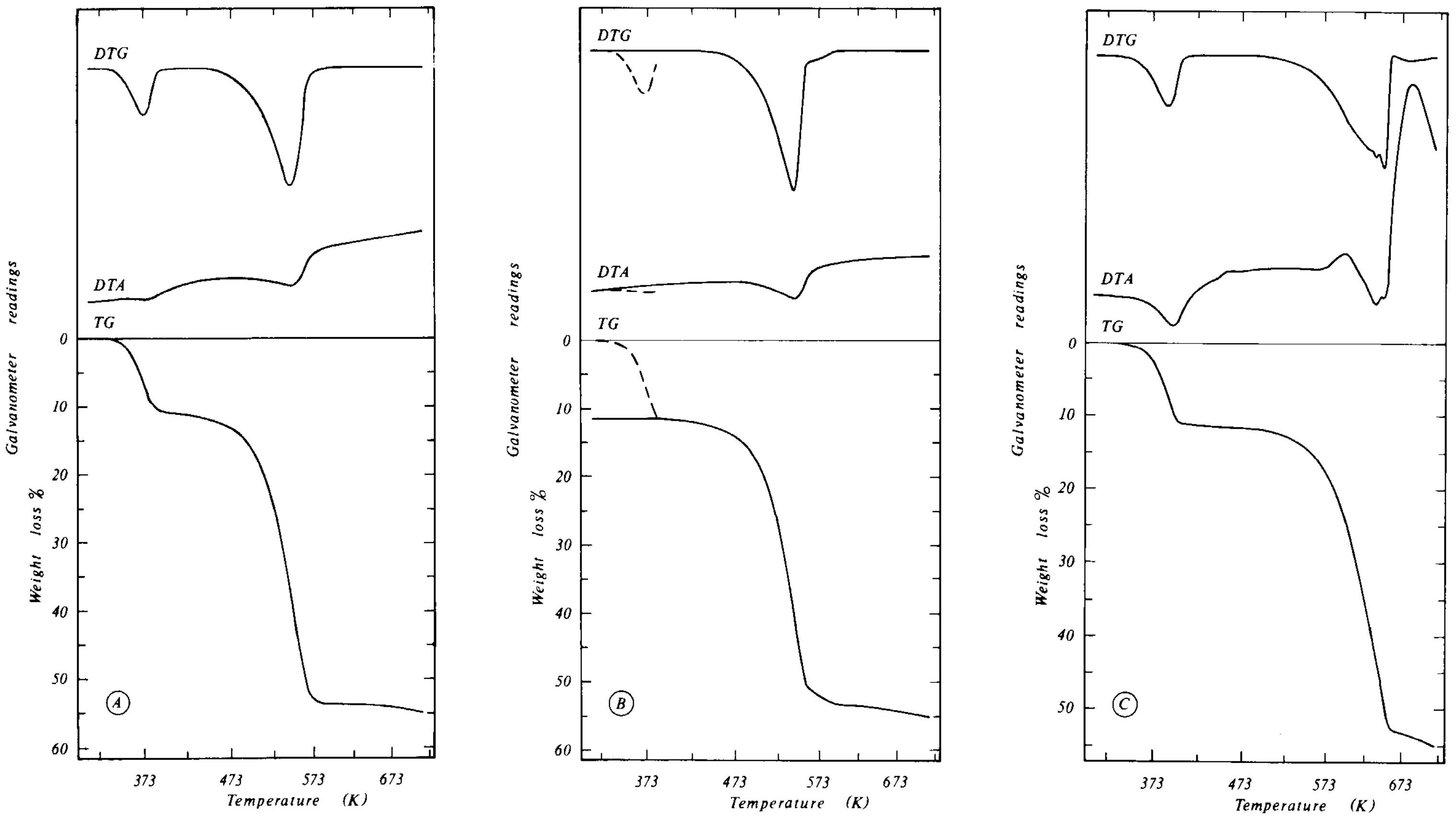

Fig. 1. Thermal analyses of $[CH_3(CH_2)_5NH_3]_2PbCl_6$. A, B, $m = 80$ mg; sample holder, platinum plate; galvanometer sensitivities: DTG = 1/10, DTA = 1/5 and TG = 50 mg. C, $m = 350$ mg; sample holder, platinum crucible; galvanometer sensitivities: DTG = 1/10, DTA = 1/5 and TG = 200 mg.

RESULTS

Mono-n-alkylammonium hexachloroplumbates undergo thermal decomposition upon heating to 650 K. The decomposition runs recorded by a derivatograph for $[CH_3(CH_2)_5NH_3]_2PbCl_6$ and presented in Fig. 1 and Table 1 are characteristic for all the compounds investigated. TG and DTG curves for most compounds, $n > 2$ (Table 2), show a two-step course of thermolysis. The weight losses estimated from TG curves (Table 2) indicate that the first step corresponds to the release of one molecule of Cl_2 from one molecule of the appropriate hexachloroplumbate.

$$(C_nH_{2n+1}NH_3)_2PbCl_{6(s)} \rightarrow PbCl_{2(s)} + 2(C_nH_{2n+1}NH_3)Cl_{(s)} + Cl_{2(g)} \quad (16)$$

The second step corresponds to the sublimation (or evaporation) of two molecules of n-alkylammonium chloride from the mixture of products resulting from decomposition of one molecule of the appropriate hexachloroplumbate in step I.

$$PbCl_{2(s)} + 2(C_nH_{2n+1}NH_3)Cl_{(s)} \rightarrow PbCl_{2(s)} + 2C_nH_{2n+1}NH_{2(g)} + 2\ HCl(g) \quad (17)$$

It was found from TG curves that the final product of thermolysis is always $PbCl_{2(s)}$. Its light-grey colour, observed sometimes, suggests contamination of $PbCl_2$ with traces of carbonization products.

With an increase in the mass of the sample, the characteristic temperatures of reactions increase, as is shown in Fig. 1C. The change in the mass of the sample does not influence the course of thermolysis in the first stage. However, this usually causes the complex course of reaction (17). To avoid these effects the possibly small samples were taken for analysis.

The process of sublimation of n-alkylammonium chlorides presents a

TABLE 1

Thermal decomposition of $[CH_3(CH_2)_5NH_3]_2PbCl_6$ (cf. Fig. 1A)

α	T (K)	$d\alpha/dt$ (min^{-1})
0.1	361.5	0.0375
0.2	367.7	0.0825
0.3	371.8	0.131
0.4	374.6	0.171
0.5	377.0	0.194
0.6	378.9	0.207
0.7	381.1	0.209
0.8	383.5	0.190
0.9	387.2	0.129

TABLE 2

The thermal analyses of mono-*n*-alkylammonium hexachloroplumbates

Substance: $(C_nH_{2n+1}NH_3)_2PbCl_6$ *n*	Thermal process [a]	Weight loss (%)		Peak temperature in [2]			Temperature [2]			
		Experimental, TG	Theoretical	DTG T_m (K)	DTA T'_m (K)	$\Delta T = T_m(S) - T_m(D)$ (K)	$T_{\alpha=0.01}$ [b] (K)	$T_{\alpha=0.1}$ [c] (K)	$T_{\alpha=0.9}$ [c] (K)	$\Delta T_\alpha = T_{\alpha=0.9} - T_{\alpha=0.1}$ [c] (K)
0	D(unresolved)		16.0	495			420			
				454						
	S		23.5	517	520					
				541	545					
1	D(unresolved)	17.3	14.6	420	419		370			
					484					
	S	25.2	27.9	503	505					
				568	572					
2	D(unresolved)	16.5	13.8	409	411		355			
	S	29.3	31.8	482	484					
				538	541					

3	D	13.3	13.1	403	405			367.2	409.1	41.9
						130	355			
	S	34.7	35.4	533	535					
4	D	12.7	12.5	394	395			374.4	401.1	26.7
						141	365			
	S	38.4	38.6	535	538					
5	D	12.0	11.9	393	396			375.2	398.7	23.5
						151	370			
	S	41.1	41.5	542	545					
6	D	11.2	11.4	380	384			361.5	387.2	25.7
						161	355			
	S	44.4	44.1	541	543					
7	D	10.5	10.9	364	365			343.2	369.3	26.1
						181	340			
	S	46.0	46.5	545	546					
8	D	9.6	10.4	356	359			336.4	365.4	29.0
						200	330			
	S	48.5	48.7	556	558					

[a] D = decomposition [step I corresponding to reaction (16)]; S = sublimation [step II corresponding to reaction (17)].

[b] $T_{\alpha=0.01}$ = decomposition temperature of both reaction stages.

[c] Temperatures corresponding to the first decomposition step: $T_{\alpha=0.1}$ = temperature at the beginning of a decomposition; $T_{\alpha=0.9}$ = temperature at the end of a decomposition; ΔT_{α} = the temperature interval of a decomposition.

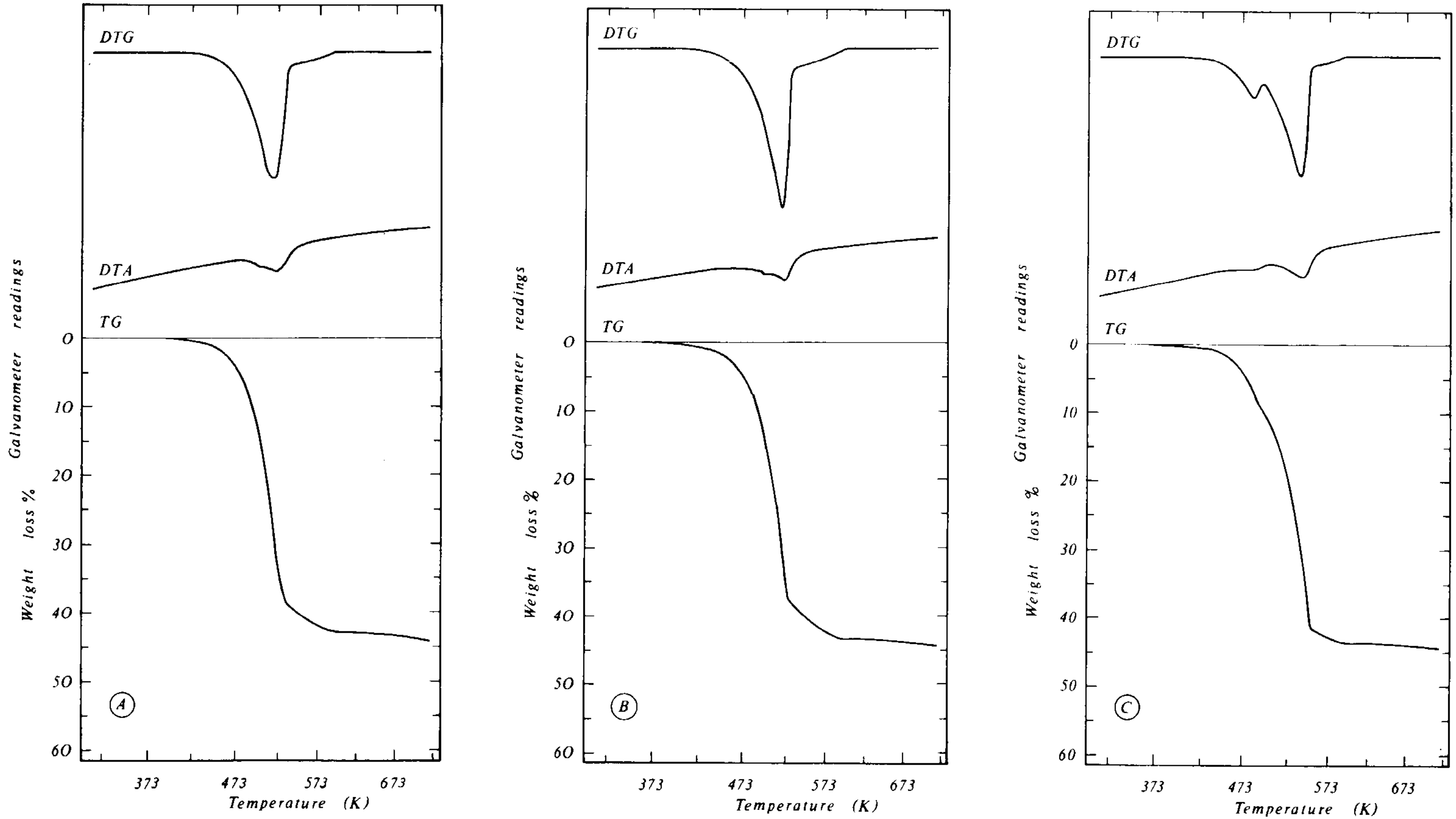

Fig. 2. Thermal analyses of $[CH_3(CH_2)_5NH_3]Cl$. $m = 35.3$ mg; sample holder, platinum plate; galvanometer sensitivities: DTG = 1/10, DTA = 1/5 and TG = 50 mg. A, Pure; B, in mixture with 35.6 mg KCl; C, in mixture with 35.6 mg $PbCl_2$.

complex problem and this will be discussed elsewhere [16]. In this work some experiments were done which could help to explain the overall course of thermolysis of hexachloroplumbates. It may be seen in Table 2 that with the exception of the first three compounds of the series, reaction (17) proceeds smoothly and it can be characterized by one endothermic peak on the DTA curve and a corresponding minimum on the DTG curve. Thermogravimetric data for any pure *n*-alkylammonium chlorides show that their transfer from the solid to the gas phase is always a one-step process (Fig. 2A) [16]. The presence of KCl, as a foreign substance, does not affect the course of this process (Fig. 2B). Instead, mixtures of $PbCl_2$ with some *n*-alkylammonium chlorides heated up to complete volatilization show additional thermal effects (Fig. 2C). To obtain additional information, alkylammonium hexachloroplumbates were heated in the oven of the derivatograph until the first step was complete. After cooling, the samples were re-analyzed. As may be seen in Fig. 1B effects due to the presence of $PbCl_2$ have not always been observed. $PbCl_2$ heated within the temperature range of interest does not undergo any thermal transformations [2,17]. The complex course of the sublimation of mono-*n*-alkylammonium chlorides is apparently due to the presence of $PbCl_2$. Nevertheless, the present knowledge of this problem does not allow one to explain this phenomenon. It is worth mentioning that similar effects have been observed earlier [7].

Other valuable information concerning thermal properties of mono-*n*-alkylammonium hexachloroplumbates is available from Table 2. 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 for other hexachloroplumbates [2,4,6,7]. Temperatures T_m and T'_m, corresponding to the first decomposition stage, reach their highest values for ammonium hexachloroplumbate and then they decrease with an increase in the length of the aliphatic chain of amine. The same direction of changes is observed for $T_{\alpha=0.9}$. Instead, temperatures T_m and T'_m, corresponding to the second reaction step, do not depend significantly on the *n* values. A very interesting dependence exists between the initial temperatures of reaction, $T_{\alpha=0.01}$ or $T_{\alpha=0.1}$, and the number of carbon atoms in the aliphatic chain of amine. Temperatures at the beginning of a decomposition reach their highest values for ammonium hexachloroplumbate and then they decrease sharply for the next two compounds of the series. Unexpectedly, an increase is observed in the values of $T_{\alpha=0.01}$ and $T_{\alpha=0.1}$ with an increase of *n*, from $n = 3$ to $n = 5$, and then they start to decrease again. The result of these changes is such that values of ΔT_α reach a minimum at $n = 5$.

It is known from the literature that free alkylamines are reactive toward Cl_2 [7,18–21]. Hence, one might expect consumption of some chlorine during the course of thermolysis of alkylammonium hexachloroplumbates. Chlorination processes are less probable in the solid phase where amines are strongly bonded with proton, forming the appropriate cations [22]. They might appear in the gas phase where interactions between amines and HCl are much weaker [23,24]. At the same time interactions between molecules of amines and Cl_2 become comparable with the former [25,26].

To examine whether chlorination processes occur or not during thermoly-

TABLE 3

Isothermal decomposition data [a]

Substance: $(C_nH_{2n+1}NH_3)_2PbCl_6$ n	Additional substance [b] (weight, mg)	V_{Ar} (cm^3 min^{-1})	T (K)	m (mg)	ν (mole%)
0		200	535	80	49.4
	NH_4Cl (160)				46.9
	$PbCl_2$ (400)				46.1
			455		58.1
	NH_4Cl (160) $PbCl_2$ (400)				48.8
		20	535		40.3
			455		27.6
1		200	535	80	91.5
			395		95.6
2		200	515	80	86.8
			395		91.9
3		200	505	80	87.0
			395		93.6
4		200	505	80	69.0
			385		87.3
5		200	505	80	67.2
			385		94.5
6		200	525	80	79.7
	$[CH_3(CH_2)_5NH_3]Cl$ (160)				51.0
	$PbCl_2$ (400)				78.3
			375		95.9
	$[CH_3(CH_2)_5NH_3]Cl$ (160)				82.6
	$PbCl_2$ (400)				93.6
		20	525		61.2
			375		84.8
7		200	525	80	73.9
			355		88.3
8		200	545	80	76.5
			345		93.5

[a] V_{Ar} is the Argon flow rate through the reactor. T is the temperature of thermolysis. For the given substance the thermolysis temperatures were taken from DTG curves. They correspond approximately to the maximum weight losses (cf. Table 2). m is the sample weight. ν is the mole % of liberated oxidants, determined by the analytical ratio of the number of moles of oxidant trapped in the KI absorbers to the number of moles of Pb(IV) in the reactant.

[b] Additional substances were placed as a layer covering the reactant.

sis of alkylammonium hexachloroplumbates, we performed experiments in the quartz reactor (Fig. 1b in ref. 6), thus permitting the quantitative estimation of amounts of liberated chlorine. The results of these investigations, presented in Table 3, indicate that carrying out the decomposition at temperatures corresponding to the first step generally enables more than 90% of the chlorine resulting from the Pb(IV) content in the substrate to be trapped in the KI absorber. In comparison, in experiments performed at temperatures corresponding to the second step the amounts of oxidant (ν) carried off from the reaction zone are significantly lower. Values of ν generally decrease with a decrease in the flow rate of the inert gas through the reactor and in the presence of the appropriate amine hydrochlorides. However, when compounds were covered with a layer of a foreign substance ($PbCl_2$), the values of ν were only slightly lower than those obtained for pure compounds.

The foregoing facts together with the thermal analysis data (Table 2) lead to the conclusion that chlorination processes occur in the gas phase. When the reaction stages are markedly separate from one another in the temperature scale used (ΔT values in Table 2), the chlorine liberated in the first step is removed from the reaction zone before the appropriate *n*-alkylammonium chlorides start to sublime. This course of reaction is typical for most of the compounds investigated ($n > 2$) and it is characteristic for experiments conducted at linear temperature increase conditions and moderate heating rates. However, the first three compounds of this series show different behaviour. Two decomposition steps are partially overlapped, in the case of $(CH_3NH_3)_2PbCl_6$ and $(C_2H_5NH_3)_2PbCl_6$, or completely overlapped, as is observed for $(NH_4)_2PbCl_6$. It causes consumption of some chlorine in secondary processes.

Since the second step of thermolysis of alkylammonium hexachloroplum-

TABLE 4

Heats of thermal decomposition of mono-*n*-alkylammonium hexachloroplumbates [a]

Substance: $(C_nH_{2n+1}NH_3)_2PbCl_6$ n	ΔH_d^0 (J mole^{-1})	Const.	Correlation coefficient, $\lvert r\rvert$
3	6.75×10^4	19.9	0.9990
4	1.10×10^5	33.1	0.9967
5	1.25×10^5	37.9	0.9970
6	1.11×10^5	34.6	0.9992
7	9.66×10^4	31.6	0.9965
8	8.30×10^4	27.6	0.9959

[a] The enthalpies of decomposition (ΔH_d^0) and const. values were calculated from eqn. (1), within a range of α values from 0.2 to 0.7.

TABLE 5

Kinetic parameters for the thermal decomposition of $[CH_3(CH_2)_5NH_3]_2PbCl_6$

Symbol [c] of the mechanism	Method of evaluation of kinetic constants [a]					
	A: eqn. (8)			B: eqn. (9)		
	E	Z	$\lvert r \rvert$	E	Z	$\lvert r \rvert$
R1	9.70 4	8.30 10	0.98908	1.00 5	7.24 09	0.98978
R2	1.15 5	1.75 13	0.99696	1.18 5	1.29 12	0.99713
R3	1.22 5	1.15 14	0.99837	1.25 5	8.02 12	0.99846
P1	7.12 4	1.96 07	0.98857	7.43 4	2.32 06	0.98955
P2	6.26 4	1.18 06	0.98830	6.57 4	1.59 05	0.98944
P3	4.54 4	4.01 03	0.98745	4.85 4	7.47 02	0.98908
E1						
B1						
P4	1.96 4	5.56 −01	0.98298	2.27 4	2.40 −01	0.98745
F1	1.36 5	5.24 16	0.99920	1.40 5	3.24 15	0.99923
A2	6.51 4	3.85 06	0.99913	6.82 4	5.00 05	0.99920
A3	4.13 4	1.31 03	0.99905	4.45 4	2.68 02	0.99916
D1	2.00 5	1.61 25	0.98978	2.03 5	6.80 23	0.99010
D2	2.22 5	1.13 28	0.99476	2.25 5	4.30 26	0.99491
D3	2.49 5	2.47 31	0.99846	2.53 5	8.36 29	0.99850
D4	2.31 5	5.15 28	0.99639	2.34 5	1.89 27	0.99649

Symbol of the mechanism	Method of evaluation of kinetic constants [a]		
	E: eqn. (12)		
	E	Z	δ
R1	1.01 5	9.52 09	0.089069
R2	1.19 5	1.81 12	0.056274
R3	1.25 5	8.80 12	0.044105
P1	7.49 4	2.79 06	0.067760
P2	6.62 4	1.85 05	0.060522
P3	4.88 4	8.17 02	0.045843
E1	−1.40 5	−4.55 −24	−0.23719
B1	1.53 5	−8.67 17	−2.2293
P4	2.28 4	2.47 −01	0.023320
F1	1.40 5	3.70 15	0.035771
A2	6.82 4	4.93 05	0.017789
A3	4.45 4	2.72 02	0.011833
D1	2.08 5	2.99 24	0.16792
D2	2.29 5	1.55 27	0.13484
D3	2.54 5	1.34 30	0.085828
D4	2.37 5	4.87 27	0.11781

[a] Calculations were performed on a TI 59 calculator. Values are presented in computer notation, e.g. −5.00 −05 = -5.00×10^{-5}. E = apparent activation energy (J mole^{-1}); Z = constant (s^{-1}); $|r|$ = correlation coefficient; δ represents values of the statistical function given by eqn. (16).

C: eqn. (10)			D^{b}: eqn. (11)		
E	*Z*	δ	*E*	*Z*	δ
9.81 4	1.18 11	0.089241	9.83 4	1.34 11	0.089221
1.16 5	2.58 13	0.056495	1.16 5	2.71 13	0.056404
1.22 5	1.32 14	0.044214	1.22 5	1.38 14	0.044222
7.18 4	2.38 07	0.067947	7.21 4	2.84 07	0.067921
6.31 4	1.39 06	0.060711	6.33 4	1.62 06	0.060682
4.57 4	4.43 03	0.046035	4.60 4	5.54 03	0.045997
−1.44 5	5.83 −23	0.23736	−1.44 5	5.57 −23	0.23737
1.50 5	−1.59 19	−2.2290	1.50 5	−1.66 19	−2.2290
1.97 4	5.78 −01	0.023518	2.03 4	9.21 −01	0.023451
1.36 5	4.47 16	0.035695	1.37 5	6.49 16	0.035675
6.51 4	3.81 06	0.017698	6.54 4	4.60 06	0.017711
4.13 4	1.29 03	0.011744	4.17 4	1.69 03	0.011759
2.05 5	7.52 25	0.16808	2.05 5	7.74 25	0.16807
2.26 5	4.30 28	0.13500	2.26 5	4.42 28	0.13499
2.51 5	4.12 31	0.085921	2.51 5	4.22 31	0.085927
2.34 5	1.40 29	0.11795	2.34 5	1.43 29	0.11795

F: eqn. (13)			G: eqn. (14)		
E	*Z*	δ	*E*	*Z*	δ
7.34 4	3.75 07	0.27541	7.64 4	3.85 06	0.27527
1.16 5	2.36 13	0.16687	1.19 5	1.58 12	0.16671
1.31 5	2.20 15	0.12799	1.34 5	1.31 14	0.12782
4.58 4	5.08 03	0.25999	4.87 4	7.74 02	0.25986
3.66 4	2.55 02	0.25474	3.95 4	4.73 01	0.25460
1.84 4	6.51 −01	0.24405	2.11 4	1.99 −01	0.24393
−3.59 4	5.66 −08	0.21064	−3.19 4	−2.21 −08	−0.21045
5.64 4	9.03 05	0.053553	5.94 4	1.18 05	0.053749
−8.86 3	6.55 −05	0.22759	−4.58 3	−5.54 −04	−0.22714
1.60 5	9.44 19	0.051585	1.63 5	4.64 18	0.051472
8.88 4	7.63 09	0.049042	9.18 4	6.56 08	0.048876
6.49 4	2.63 06	0.049663	6.78 4	2.93 05	0.049492
1.86 5	1.44 23	0.33172	1.89 5	6.13 21	0.33159
2.20 5	5.50 27	0.26286	2.24 5	2.72 26	0.26272
2.90 5	1.32 37	0.091019	2.93 5	3.64 35	0.090902
2.34 5	1.24 29	0.22665	2.37 5	4.22 27	0.22651

[b] Values of the p(x) function were calculated from 10 truncated parts of a Legendre series [ref. 14, eqn. (18)].

[c] Ref. 2, Table 1.

TABLE 6

Kinetic parameters for thermal decomposition of mono-*n*-alkylammonium hexachloroplumbates

Substance: $(C_nH_{2n+1}NH_3)_2$-$PbCl_6$ *n*	Symbol[c] of the mechanism	Method of evaluation of kinetic constants[a]								
		A: eqn. (8)			B: eqn. (9)			C: eqn. (10)		
		E	*Z*	|*r*|	*E*	*Z*	|*r*|	*E*	*Z*	*δ*
3	R2	7.12 4	3.43 06	0.99988	7.44 4	4.23 05	0.99989	7.12 4	3.45 06	0.011280
	R3	7.54 4	9.50 06	0.99975	7.86 4	1.10 06	0.99975	7.54 4	9.46 06	0.017224
	F1	8.47 4	6.35 08	0.99734	8.79 4	6.58 07	0.99749	8.47 4	6.40 08	0.064276
	D3	1.57 5	2.94 17	0.99975	1.61 5	1.64 16	0.99976	1.57 5	2.70 17	0.035355
4	R2	1.17 5	8.35 12	0.99613	1.20 5	6.27 11	0.99636	1.17 5	9.28 12	0.063911
	R3	1.24 5	5.40 13	0.99806	1.27 5	3.82 12	0.99818	1.24 5	6.09 13	0.048238
	F1	1.39 5	2.35 16	0.99986	1.42 5	1.48 15	0.99987	1.39 5	2.43 16	0.014960
	D3	2.54 5	5.69 30	0.99818	2.57 5	1.97 29	0.99823	2.55 5	8.64 30	0.094077
5	R2	1.33 5	1.89 15	0.99555	1.37 5	1.24 14	0.99576	1.34 5	2.29 15	0.068280
	R3	1.41 5	1.65 16	0.99763	1.46 5	1.02 15	0.99775	1.42 5	2.06 16	0.053063
	F1	1.59 5	1.41 19	0.99977	1.62 5	7.77 17	0.99978	1.59 5	1.54 19	0.019132
	D3	2.89 5	4.65 35	0.99775	2.92 5	1.41 34	0.99780	2.91 5	8.58 35	0.10222
6	R2	1.15 5	1.75 13	0.99696	1.18 5	1.29 12	0.99713	1.16 5	2.58 13	0.056495
	R3	1.22 5	1.15 14	0.99837	1.25 5	8.02 12	0.99846	1.22 5	1.32 14	0.044214
	F1	1.36 5	5.24 16	0.99920	1.40 5	3.24 15	0.99923	1.36 5	4.47 16	0.035695
	D3	2.49 5	2.47 31	0.99846	2.53 5	8.36 29	0.99850	2.51 5	4.12 31	0.085921
7	R2	1.01 5	1.07 12	0.99864	1.04 5	8.47 10	0.99873	1.01 5	9.88 11	0.038652
	R3	1.07 5	5.83 12	0.99919	1.10 5	4.38 11	0.99923	1.07 5	5.59 12	0.031441
	F1	1.20 5	1.75 15	0.99827	1.23 5	1.17 14	0.99834	1.20 5	1.71 15	0.051956
	D3	2.20 5	6.49 28	0.99923	2.23 5	2.37 27	0.99925	2.20 5	6.15 28	0.062194
8	R2	8.68 4	1.28 10	0.99325	8.98 4	1.17 09	0.99372	8.71 4	1.42 10	0.082460
	R3	9.21 4	5.91 10	0.99599	9.50 4	5.08 09	0.99626	9.23 4	6.31 10	0.067759
	F1	1.04 5	1.23 13	0.99932	1.07 5	9.39 11	0.99937	1.04 5	1.34 13	0.031952
	D3	1.90 5	7.54 24	0.99626	1.93 5	3.14 23	0.99639	1.91 5	1.05 25	0.13021

Substance: (C_nH_{2n+1}-NH_3)$_2$-$PbCl_6$	Symbol [c] of the mechanism	Method of evaluation of kinetic constants [a]											
		D [b]: eqn. (11)			E: eqn. (12)			F: eqn. (13)			G: eqn. (14)		
n		E	Z	δ	E	Z	δ	E	Z	δ	E	Z	δ
3	R2	7.14 4	4.00 06	0.011256	7.44 4	4.22 05	0.011076	7.12 4	3.63 06	0.049855	7.43 4	3.95 05	0.049894
	R3	7.56 4	1.09 07	0.017293	7.86 4	1.09 06	0.017700	8.05 4	4.88 07	0.061455	8.36 4	4.75 06	0.061886
	F1	8.49 4	7.33 08	0.064345	8.79 4	6.58 07	0.064819	1.00 5	7.94 10	0.15772	1.03 5	6.12 09	0.15824
	D3	1.57 5	2.81 17	0.035499	1.60 5	1.41 16	0.036065	1.82 5	8.23 20	0.17503	1.85 5	3.58 19	0.17552
4	R2	1.17 5	9.78 12	0.063898	1.20 5	6.49 11	0.063726	1.01 5	6.54 10	0.10842	1.04 5	4.99 09	0.10825
	R3	1.24 5	6.40 13	0.048211	1.27 5	4.02 12	0.048035	1.18 5	9.63 12	0.067808	1.21 5	6.34 11	0.067584
	F1	1.39 5	2.54 16	0.014948	1.42 5	1.43 15	0.014898	1.50 5	7.65 17	0.030553	1.54 5	5.42 16	0.030775
	D3	2.55 5	8.86 30	0.094059	2.58 5	2.77 29	0.093871	2.80 5	2.57 34	0.033387	2.83 5	7.35 32	0.033293
5	R2	1.34 5	2.39 15	0.068266	1.37 5	1.40 14	0.068130	1.13 5	5.05 12	0.10971	1.16 5	2.32 11	0.10958
	R3	1.42 5	2.15 16	0.053035	1.45 5	1.19 15	0.052892	1.30 5	5.05 14	0.072096	1.33 5	3.03 13	0.071990
	F1	1.59 5	1.61 19	0.019102	1.62 5	7.94 17	0.019013	1.66 5	1.42 20	0.038854	1.69 5	6.75 18	0.038935
	D3	2.91 5	8.77 35	0.10221	2.94 5	2.41 34	0.10206	3.14 5	1.41 39	0.053368	3.18 5	4.89 37	0.053272
6	R2	1.16 5	2.71 13	0.056404	1.19 5	1.81 12	0.056274	1.16 5	2.36 13	0.16687	1.19 5	1.58 12	0.16671
	R3	1.22 5	1.38 14	0.044222	1.25 5	8.80 12	0.044105	1.31 5	2.20 15	0.12799	1.34 5	1.31 14	0.12782
	F1	1.37 5	6.49 16	0.035675	1.40 5	3.70 15	0.035771	1.60 5	9.44 19	0.051585	1.63 5	4.64 18	0.051472
	D3	2.51 5	4.22 31	0.085927	2.54 5	1.34 30	0.085828	2.90 5	1.32 37	0.091019	2.93 5	3.64 35	0.090902
7	R2	1.02 5	1.48 12	0.038704	1.04 5	7.98 10	0.038517	9.92 4	5.85 11	0.13239	1.02 5	4.25 10	0.13222
	R3	1.07 5	5.90 12	0.031487	1.10 5	4.26 11	0.031437	1.12 5	3.30 13	0.092549	1.15 5	2.28 12	0.092388
	F1	1.20 5	1.79 15	0.051949	1.23 5	1.16 14	0.052192	1.38 5	8.19 17	0.048531	1.41 5	4.64 16	0.048617
	D3	2.20 5	6.31 28	0.062203	2.23 5	2.28 27	0.062191	2.51 5	2.92 33	0.073697	2.54 5	9.27 31	0.073757
8	R2	8.73 4	1.62 10	0.082429	9.00 4	1.28 09	0.082173	7.30 4	1.11 08	0.16265	7.58 4	1.07 07	0.16240
	R3	9.25 4	7.19 10	0.067728	9.52 4	5.39 09	0.067470	8.50 4	5.13 09	0.12514	8.78 4	4.31 08	0.12488
	F1	1.04 5	1.41 13	0.031896	1.07 5	1.05 12	0.031702	1.09 5	7.50 13	0.047936	1.12 5	5.32 12	0.047610
	D3	1.91 5	1.08 25	0.13020	1.94 5	4.49 23	0.12995	2.08 5	4.45 27	0.10976	2.10 5	1.21 26	0.10950

bates, i.e. sublimation of the appropriate amine hydrochlorides from the mixture of products resulting from the first step, may be complicated by the presence of $PbCl_2$, we have decided to investigate this problem separately [16]. In this work the thermodynamics and kinetics of the first step, described by reaction (16), were examined.

For the first three compounds of the series decomposition stages are not separate enough to evaluate the kinetic variables, α, T and $d\alpha/dt$, from thermal analysis curves. Hence, thermodynamic and kinetic considerations were conducted only for $(C_nH_{2n+1}NH_3)_2PbCl_6$, with $n = 3–8$.

The enthalpies of the thermal decomposition estimated from eqn. (1) are listed in Table 4. Values of both ΔH_d^0 and the constant increase with an increase in the length of the aliphatic chain of the amine up to $n = 5$ and then they apparently decrease. It is worth mentioning that a reverse dependence is observed in the case of ΔT_α values.

The kinetic parameters were evaluated by methods which have been described previously. As an example we present in Table 5 values of kinetic parameters and statistical functions for the thermal decomposition of *n*-hexylammonium hexachloroplumbate. The compounds investigated belong to the same class of derivatives of chloroplumbic acid. Furthermore, the only factor differentiating them is probably the length of the aliphatic chain of the amine. Therefore, one might expect the same thermal decomposition mechanism for all mono-*n*-alkylammonium hexachloroplumbates. Indeed, analyzing the results of calculations, it was found that the relative differences of values of the correlation coefficients and δ functions are similar for any hexachloroplumbate. This fact would confirm the correctness of the foregoing assumption.

In searching for an adequate mechanism of the thermal process, i.e. the form of functions $g(\alpha)$ or $f(\alpha)$, we applied criteria which had been established previously [2,13]. Based on these criteria, which in the ideal case require $|r|$ values to be equal to 1 and δ values to be equal to 0, we selected four mechanisms: R2, R3, F1 and D3. Also, functions $g(\alpha)$ and $f(\alpha)$ corresponding to the symbols A2 and A3 satisfy the foregoing criteria very well. These mechanisms are, however, less probable since values of activation energies corresponding to them are far below the appropriate ΔH_d^0 values for the decomposition process. Therefore, we do not consider A2 and A3 mechanisms in further discussion. For the chosen reaction mechanisms, values of kinetic constants together with values of statistical functions $|r|$ and δ are listed in Table 6

For any $f(\alpha)$ or $g(\alpha)$ function, thermodynamic parameters (Table 4), ΔT_α values (Table 2) and kinetic constants show similar dependence on the size of the organic cation, i.e. they have their highest values at $n = 5$. Moreover, our data shows that the higher the ΔH_d^0 or E values, the lower the temperature interval (ΔT_α) of a decomposition.

DISCUSSION

To describe the thermal stability of a solid substance three simple characteristics may be applied [27,28]: (a) enthalpy of the thermal decomposition (ΔH_d^0), (b) activation energy (E) and (c) any temperature limits of the thermal reaction (T_m, T'_m, T_α, ΔT_α). These parameters represent respectively, thermodynamic, kinetic and temperature characteristics of the thermal stability.

If one considers the thermal stability of a given substance as an ability to resist decomposition upon rising temperature, then the temperature of the onset of reaction, or temperature of the maximum rate of reaction may be considered as the first parameters describing this feature. ΔH_d^0 and E values probably provide the most adequate characteristics of the thermal stability. The qualitative rule is that the higher the ΔH_d^0 or E values, the higher the thermal stability of a given substance. The foregoing characteristics indicate that ammonium hexachloroplumbate shows the highest thermal stability among the compounds investigated. The thermal stability of the other compounds in the series changes with the length of the aliphatic chain of the amine and the direction of these changes is best demonstrated by changes in $T_{\alpha=0.1}$ values with n (Table 2).

Presumably at least three factors determine the thermal stability of alkylammonium hexachloroplumbates. All of them result from the properties of the appropriate alkylamines.

Since hexachloroplumbates are considered as salt-like compounds it may be expected that their thermal stability is dependent on the basicity of amines. The basicity in the series of mono-*n*-alkylamines increases markedly from ammonia to methylamine and then it increases only slightly with an increase in the length of the aliphatic chain of the amine [22,29,30]. The energy of the bond formed between the proton and amine should increase with an increase of the basicity of the amine [22]. If interactions between the alkylammonium cation and the $PbCl_6^{2-}$ anion would be the same for any amine one could expect the thermal stability of hexachloroplumbates to be directly proportional to the basicity of amine. In reality the reverse dependence is observed. This means that factors other than basicity of amines determine thermal properties of alkylammonium hexachloroplumbates.

The second factor describing the thermal properties of alkylammonium hexachloroplumbates might arise from the size of the cation. Kapustinskii and Vaver [31,32] proposed a simple equation which relates the lattice energies and heats of formation of hexachloroplumbates with some parameters, among others, with the size of the cation. Although Kapustinskii's equation is oversimplified, it could give some qualitative information on the stability of hexachloroplumbates. Unfortunately, this equation predicts an increase of the thermal stability of hexachloroplumbate with an increase of the size of the cation, whereas experimentally the reverse order was found.

The third and presumably the most important factor determining thermal properties of hexachloroplumbates is the structure of the cation. Kapustinskii's equation [32] may be applied mainly in the case of cations having approximately spherical structure, i.e. for metal cations or tetrahedral ammonium cations having four identical substituents. Mono-*n*-alkylammonium cations are characterized by highly unsymmetrical structures and this is probably responsible for the atypical properties of their salts with the $PbCl_6^{2-}$ anion. Undoubtedly, the decrease in the symmetry of the cation makes the formation of the crystal lattice more difficult. It should lead to a decrease in the lattice energy and, consequently, a decrease in the heat of formation of a given hexachloroplumbate. The effect described may explain the decrease of the thermal stability in the order $(NH_4)_2PbCl_6 > (CH_3NH_3)_2PbCl_6 > (C_2H_5NH_3)_2PbCl_6$. With an increase in the length of the aliphatic chain of the amine, the hydrocarbon part of a molecule becomes predominant and, hence, it may determine the structure and thermal properties of mono-*n*-alkylammonium salts. Indeed, it was established that some complexes containing long chain *n*-alkylamines are characterised by a "sandwich structure" made up of the regular alternation of inorganic and hydrocarbon layers [33]. Therefore, one may expect an increase in the importance of this factor in determination of the thermal behaviour of mono-*n*-alkylammonium hexachloroplumbates with an increase in the length of the hydrocarbon chain. The appearance of the layer structures would lower the lattice energy and, consequently, the thermal stability. Indeed, similar relations have been reported in the thermal decomposition studies of some complexes containing long-chain *n*-alkylamines [34]. However, it still remains inexplicable why thermal stability increases when n changes from 3 to 5. We do not fully understand this discrepancy, but a possible explanation might be that hydrocarbon chains of these amines take some favourable shapes in the crystal lattice which lower the lattice energy.

The kinetic information listed in Tables 5 and 6 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. In the case of the F1 mechanism, describing a unimolecular decay law, the highest values of the correlation coefficients, as well as the lowest δ values were obtained.

Comparing the thermal decomposition of mono-*n*-alkylammonium hexachloroplumbates with that of alkali metal hexachloroplumbates [2], a difference is noticed in the equation describing the kinetics of this process. The thermal decomposition of alkali metal hexachloroplumbates has been well described by an R2 mechanism with activation energies only slightly exceeding the appropriate ΔH_d^0 values [2]. Instead, an F1 mechanism, describing the most probable kinetics of the thermal decomposition of alkylammonium hexachloroplumbates, requires considerably higher activation energies. Two identical products are formed in the thermal decomposition of both groups of compounds, namely $PbCl_{2(s)}$ and $Cl_{2(g)}$. The only difference arises from other chlorides. Therefore, it might suggest that during thermolysis of mono-*n*-alkylammonium hexachloroplumbates, the formation of a new solid phase of the appropriate *n*-alkylammonium chloride is the rate-determining process.

One of the main aims of this work is to confirm that eqns. (6) and (7) may be applied in the description of the solid-state reaction kinetics. For this purpose we compare the relationships given by eqns. (6) and (7) with the kinetic equations (2) and (3) which are widely recommended for use in the description of solid-state reaction kinetics. The results of kinetic calculations listed in Tables 5 and 6 show some regularities.

Comparing the results of calculations performed based on methods A and B, it is seen that correlation coefficients obtained for any experimental data points and any function $g(\alpha)$ reach higher values in the case of eqn. (7). This means that linearization procedures based on the integral equation proposed by the authors [13] give better fits to the experimental data than those based on the method of Coats and Redfern [15].

It is not possible to compare integral eqns. (3) and (7) directly, by applying linearization procedures, since the former equation cannot be rearranged to the linear form. Thus, we performed calculations based on the statistical function δ. Values of the δ function found for methods C, D and E indicate again that eqn. (7) is a better interpolation formula than are eqns. (3) and (5). Using eqn. (7) usually gives lower values for the δ function than eqns. (3) and (5). Equation (11) is accurate from the mathematical point of view, whereas eqn. (10) is based on Coats and Redfern's approximation. Hence, one might expect lower δ values in the case of method D. The results of calculations indicate, however, that this is not always observed.

In the case of methods F and G it is seen that generally lower values of δ are observed for differential eqn. (6). This means that the differential equation proposed by the authors [13] is a better interpolation formula than that widely recommended in the literature [eqn. (2)].

Comparing values of δ for differential and integral methods it is noticed that much higher values were obtained for the former methods. Presumably this results from experimental uncertainties whose significance become more important in the case of differential methods. Most functions describing the reaction mechanism values *E* and *Z* are slightly higher if one uses differential methods, Nevertheless, the agreement between kinetic parameters derived from differential and integral methods is quite good considering that values of *E* and *Z* result from application of different forms of kinetic equations and slightly different experimental data.

The kinetic equations proposed by the authors [13] have simple mathematical forms and are easy to work with. Moreover, the foregoing facts indicate that they also give a better fit to the experimental data than do other equations which are widely proposed in the literature. Therefore, the authors fully recommend them for use in the description of non-isothermal reaction kinetics.

ACKNOWLEDGEMENT

The authors would like to thank Mrs. Irena Nikel for experimental assistance.

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