Thermochimica Acta, 46 (1981) 147—166
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL REACTIONS OF LEAD(IV) CHLORIDE COMPLEXES IN THE SOLID STATE. PART IV. THERMOLYSIS OF ALKALI METAL HEXACHLOROPLUMBATES

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(Received 2 December 1980)

ABSTRACT

Alkali metal hexachloroplumbates of general formula $M_2(I)PbCl_6$, with M(I) = K, Rb, Cs, undergo thermal decomposition on heating to 700 K. The thermal processes in the solid state have been studied by differential thermal analysis (DTA) and thermogravimetry (TG) with a derivatograph. The thermolysis occurs in one step

$$M_2(I)PbCl_6 \rightarrow 2\ M(I)Cl_{(s)} + PbCl_{2(s)} + Cl_{2(g)}$$

The experimental TG and DTG curves were used to estimate the enthalpy of thermal dissociation. Based on these curves the kinetic parameters of thermolysis have been evaluated. In the linearization procedure of the kinetic equation

$$d\alpha/dT = A/\Phi \cdot f(\alpha) \cdot \exp(-E/RT)$$

the methods of Freeman and Carroll, Coats and Redfern, Horowitz and Metzger and Gorbachev were applied. Sixteen $f(\alpha)$ functions which describe the primary mechanism of thermal decomposition of solid substances — nucleation, growth of nuclei, phase boundary reactions and diffusion processes — were used in the least squares error analysis. The dehydration of calcium oxalate monohydrate was performed to confirm the validity of the analytical and computational procedures. The differences in values of the kinetic and thermodynamic parameters for hexachloroplumbates thermolyses have been discussed. It was found that K_2PbCl_6 showed atypical thermal properties. This is probably caused by the different crystal structure of K_2PbCl_6 as compared with those of Rb_2PbCl_6 and Cs_2PbCl_6, as well as the abnormal course of its thermolysis. The thermal properties of alkali metal hexachloroplumbates have been compared with those for analogous compounds of the type $M_2(I)M(IV)X_6$ (M(IV) = Pt, Te, Tc; X = Cl, Br).

INTRODUCTION

Alkali metal chloroplumbates are the simplest and most well-known solid derivatives of hexachloroplumbic acid [1]. These compounds have properties of typical inorganic salts. Their thermal stability is limited, however, just in the case of other derivatives of chloroplumbic acid [1—4]. Alkali metal hexachloroplumbates undergo slow decomposition at room temperature, gradually losing chlorine, and thus their oxidative power [1].

A number of properties of these compounds are known [1]. Many parameters have been established based on crystallographic [5—8], IR and Raman [8—15] and NQR [6,16] measurements. To our knowledge, only limited investigations of the thermal behaviour of alkali metal hexachloroplumbates have been carried out [1,6,17].

In a continuation of studies on the thermal properties of solid complexes of $PbCl_4$ and H_2PbCl_6 [2—4] we decided to investigate the thermolysis of alkali metal hexachloroplumbates. Because of the uncomplicated structure of these compounds a simple course of the thermolyses could be expected, which was hopeful for the use of the experimental thermal analysis data to evaluate the kinetic and thermodynamic parameters for thermal decomposition processes. In the case of previously investigated compounds [2—4] such an approach was impossible because of the complex nature of the thermolyses.

EXPERIMENTAL

Hexachloroplumbic acid and its alkali metal salts were prepared by methods described previously [1,2].

Calcium oxalate monohydrate, supplied by Monikon (Hungary), was used without further purification as a standard substance to verify the proper working of the derivatograph.

Thermal analyses were performed on a Monikon OD-103 derivatograph. The experimental conditions are listed in Table 2. α-Al_2O_3 served as reference.

MATHEMATICAL TREATMENT OF THE THERMAL ANALYSIS DATA

The kinetic and thermodynamic constants of thermolysis were evaluated from some parameters determined from the thermal analysis results (Fig. 1).

All length measurements were done with accuracy better than 0.1 mm. In the case of temperature, distances between lines marked every 10 K were measured. Because of the non-linear scale, the appropriate intermediate temperatures were calculated based on linear extrapolation. The peak areas above the DTG curves were measured by the cut and weight technique. TG and DTG data were taken into account to estimate the degree of conversion, α. The appropriate mean α values, obtained from both TG and DTG curves, were used in further calculations. For each experimental run 11 values of α, $d\alpha/dt$ and T were chosen for the range of values of the degree of conversion between 0.1 and 0.9.

Enthalpy of the thermal reactions

The enthalpies of thermal dissociation (ΔH^0_d) of alkali metal hexachloroplumbates were estimated using an approximate method proposed by Stepin et al. [18], who used the van't Hoff equation for reactions of solid substances which take place upon dynamic temperature changes. This approach seems to be correct for dissociation processes appearing in a narrow layer adjacent to the interface (as in the case of phase boundary reactions). Under quasi-isobaric conditions it is possible to assume, over a short time interval, that it is an equilibrium reaction corresponding to T = const. Then, based on the thermodynamic equilibrium constant the following equation can be derived

$$\ln \alpha = -\Delta H_d^0/T + \text{const.} \quad (1)$$

The above method has been successfully used for estimation of the enthalpy of dissociation of many compounds [19]. Similar approaches have been proposed by other authors to evaluate the heat of dissociation based on measurements of equilibrium pressures of gaseous products upon thermolysis of solid substances [20,21]. Like methods have also been applied for estimation of the enthalpy of evaporation [22] and sublimation [23].

Kinetic parameters

The widely recommended equation for the description of reaction kinetics in the solid state can be written in the form [24,25]

$$\mathrm{d}\alpha/\mathrm{d}t = Z \cdot \mathrm{f}(\alpha) \cdot \exp(-E/RT) \quad (2)$$

In dynamic experiments with increasing temperature [24,26,27]

$$\mathrm{d}\alpha/\mathrm{d}T = Z/\Phi \cdot \mathrm{f}(\alpha) \cdot \exp(-E/RT) \quad (3)$$

where α is the degree of conversion, $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of reaction, Z is a constant (usually referred to as the frequency factor, by analogy to gas phase reactions), Φ (equal to $\mathrm{d}T/\mathrm{d}t$) is the linear heating rate, E is the apparent activation energy, and $\mathrm{f}(\alpha)$ is a function which represents the hypothetical model of the reaction mechanism.

For evaluation of kinetic parameters E and Z, four independent methods were used, allowing linearization of eqn. (3).

Differential method

After transformation of both sides of eqn. (3) into logarithmic form, it can be written as

$$\frac{\Delta \ln(\mathrm{d}\alpha/\mathrm{d}T)}{\Delta \ln \mathrm{f}(\alpha)} = 1 - \frac{E}{R}\,\frac{\Delta(1/T)}{\Delta \ln \mathrm{f}(\alpha)} \quad (4)$$

If $\mathrm{f}(\alpha) = (1-\alpha)^n$, it is possible to change eqn. (4) into the well-known and widely used form derived by Freeman and Carroll [28]. Equation (4) allows estimation of the apparent activation energy under the assumed model of the reaction mechanism. The constant Z can then be calculated based on eqn. (3). The appropriate Z values have been determined at maximum temperatures on DTG curves (T_m). The values at $\alpha = 0.9$ were used as reference points in eqn. (4). We have applied the treatment of Freeman and Carroll to 15 functions $\mathrm{f}(\alpha)$ (Table 1); however, till now this approach has been proposed in the case of $\mathrm{f}(\alpha) = (1-\alpha)^n$.

Integral methods

Equation (3) can be easily transformed into integral form

$$g(\alpha) = Z/\Phi \cdot \int_0^T \exp(-E/RT)\,\mathrm{d}t \tag{5}$$

where

$$g(\alpha) = \int_0^\alpha \mathrm{d}\alpha/f(\alpha)$$

There are no difficulties in the calculation of the integral $g(\alpha)$. The functions $g(\alpha)$, together with their differential form $f(\alpha)$, are listed in Table 1. They describe the most frequently invoked and discussed mechanisms of the thermal decomposition of the solid substances [29—34].

The right-hand side of eqn. (5) can be presented in the form

$$Z/\Phi \cdot \int_0^T \exp(-E/RT)\,\mathrm{d}T = ZE/\Phi R \cdot \int_x^\infty x^{-2}\,\mathrm{e}^{-x}\,\mathrm{d}x \tag{6}$$

where $x = E/RT$.

$\int_x^\infty x^{-2}\,\mathrm{e}^{-x}\,\mathrm{d}x$ is an example of Euler's integral which cannot be resolved exactly [35]. Among numerous approximations proposed in the analysis of reaction kinetics of solid substances, the most popular are [36]

$$\int_x^\infty x^{-2}\,\mathrm{e}^{-x}\,\mathrm{d}x = \frac{\mathrm{e}^{-x}}{x^2}\left[1 - \frac{2!}{x} + \frac{3!}{x^2} - \dots + \frac{(-1)^n(n+1)!}{x^n}\right] \tag{7}$$

and Schlömilch's approximation [37]

$$\int_x^\infty x^{-2}\,\mathrm{e}^{-x}\,\mathrm{d}x = \frac{\mathrm{e}^{-x}}{x}\left[\frac{1}{x+1} - \frac{1}{(x+1)(x+2)} + \frac{1}{(x+1)(x+2)(x+3)} - \dots\right] \tag{8}$$

Using the first two terms of approximation (7), the following equation can be derived

$$\ln\left[\frac{g(\alpha)}{T^2}\Big/\left(1 - \frac{2RT}{E}\right)\right] = \ln\frac{ZR}{\Phi E} - \frac{E}{R}\cdot\frac{1}{T} \tag{9}$$

The above equation has been proposed by Coats and Redfern [38] for functions $f(\alpha) = (1-\alpha)^n$; however, it was also successfully used in the case of another $f(\alpha)$ [30,39].

The term $\ln[1 - (2RT/E)]$ in eqn. (9) is usually neglected because for most reactions, $2RT \ll E$. This simplification gives the same equation as in the case wherein only the first term of approximation (7) is considered. In accurate calculations, eqn. (9) can be resolved by trial and error procedure.

Another approach has been proposed by Horowitz and Metzger [40], who introduced the substitution $T = T_s + \theta$, where T_s is the reference temperature

TABLE 1

Kinetic functions [29—34] used in the least squares error analysis for evaluation of the apparent activation energy (E) and the Z factor

$g(\alpha)$	$f(\alpha)$	Mechanism			
		Symbol [33]	Kinetic-controlling process [29, 34]	Description of the process [29, 34]	Equation
α	$(1-\alpha)^0$	R1	Phase boundary reactions	One-dimensional movement	Polany—Wigner
$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	R2		Two-dimensional movement (contracting area)	
$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	R3		Three-dimensional movement (contracting volume)	
$\alpha^{3/4}$	$4/3\alpha^{1/4}$	P1	Nucleation	According to the power law (spherical symmetry of nuclei)	
$\alpha^{2/3}$	$3/2\alpha^{1/3}$	P2			
$\alpha^{1/2}$	$2\alpha^{1/2}$	P3			
$\ln\alpha$	α	E1	Linear growth of nuclei	Chain	
$\ln[\alpha/(1-\alpha)]$	$\alpha(1-\alpha)$	B1		Branching	Prout—Tompkin
$\alpha^{1/4}$	$4\alpha^{3/4}$	P4	Bulk growth of nuclei	Linear, induction-stage	
$-\ln(1-\alpha)$	$(1-\alpha)$	F1		One nucleus on each particle	
$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	A2		Two-dimensional	Avrami—Erofeev
$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	A3		Three-dimensional	
α^2	$1/2\alpha^{-1}$	D1	Diffusion	One-dimensional	
$(1-\alpha)\ln(1-\alpha)+\alpha$	$[-\ln(1-\alpha)]^{-1}$	D2		Two-dimensional	
$[1-(1-\alpha)^{1/3}]^2$	$3/2(1-\alpha)^{2/3}[(1-\alpha)^{-1/3}-1]^{-1}$	D3		Three-dimensional	Jander
$1-2/3\alpha-(1-\alpha)^{2/3}$	$3/2[(1-\alpha)^{-1/3}-1]^{-1}$	D4			Ginstling—Brounshtein

(for instance: $T_{\alpha=1/e}$, T_m — temperature at maximum rate of decomposition, etc.). Then

$$\frac{1}{T} = \frac{1-(\theta/T_s)}{T_s} \tag{10}$$

because for $\theta << T_s$, $(\theta/T_s)^2 \cong 0$.

Using approximation (10), together with the first term of eqn. (7), and assuming $[1-(\theta/T_s)]^2 \cong 1$, the following equation can be derived

$$\ln g(\alpha) = \ln \frac{ZRT_s^2}{\Phi E} - \frac{E}{RT_s} + \frac{E}{RT_s^2}\,\theta \tag{11}$$

Horowitz and Metzger [40] have proposed the use of the above method in the case $f(\alpha) = \alpha^n$ and $(1-\alpha)^n$, because by the correct choice of reference temperatures it was possible to obtain a fairly simple form of the final equations.

Gorbachev [41] proposed the use of an equation which can be derived based on the first two terms of Schlömilch's approximation (8) [37]. This equation is in the form

$$\ln\left[\frac{g(\alpha)}{T}\left(\frac{E}{RT} + 2\right)\right] = \ln\frac{Z}{\Phi} - \frac{E}{R}\cdot\frac{1}{T} \tag{12}$$

It is possible to resolve the above equation only by trial and error treatment. In the first approximation the E values obtained in Coats and Redfern's method can be used to estimate values of the term $(E/RT + 2)$. Then, the left-hand side of eqn. (12) can be considered as a linear function of the reciprocal temperature.

RESULTS

Alkali metal hexachloroplumbates undergo thermal decomposition upon heating to 700 K. The decomposition run recorded by derivatograph for Rb_2PbCl_6 and presented on Fig. 1 is typical for all hexachloroplumbates. The DTA, TG and DTG curves for all investigated compounds show that their thermal decompositions are not preceded by melting or by any other transformations, and that they are one-step processes. In the case of hexachloroplumbates the weight losses estimated based on TG curves correspond to the removal of one molecule of chlorine from one molecule of substrate.

The kinetics of the thermal decomposition of solid substances are controlled by temperature and a number of other variables which determine the correlation between the degree of conversion and the time of reaction. In this work the qualitative influence of some of them on the course of thermolysis has been studied, namely, weight (volume) of sample, heating rate, shape and material of the sample holder and oven atmosphere. Because of random errors influencing thermal analysis results, all experiments were performed at least three times under established conditions. From numerous

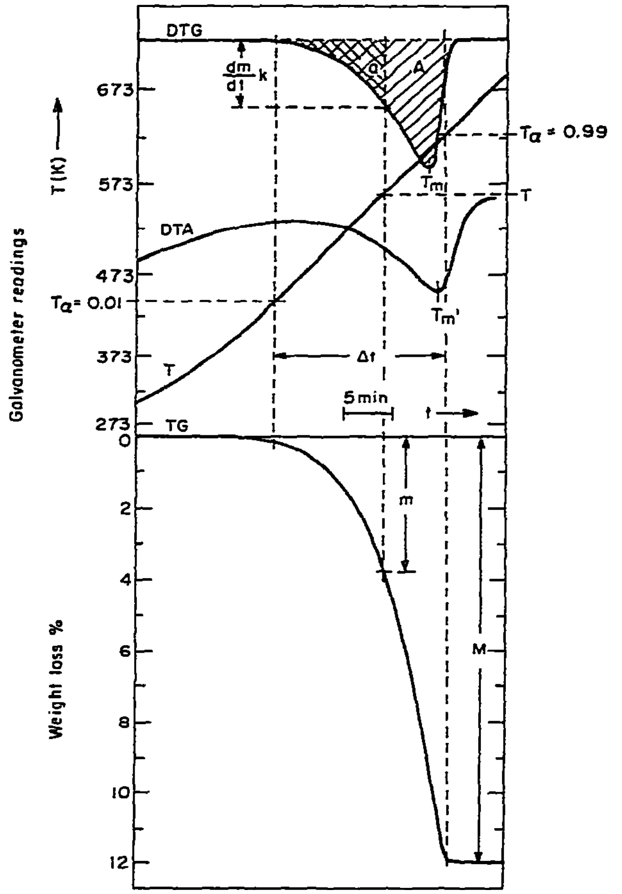

Fig. 1. Thermal analysis of Rb_2PbCl_6 (cf. Table 2, Run No. 17). $T_{\alpha=0.01}$, $T_{\alpha=0.99}$ = temperatures at the beginning and the end of decomposition, respectively; T_m = temperature at the highest rate of decomposition (maximum DTG); $T_{m'}$ = maximum temperature on the DTA curve; m = weight loss up to temperature T; M = total weight loss; $(dm/dt)k = d\alpha/dt$ = rate of weight loss at temperature T (k = constant); a, A = areas above DTG curve: a, up to temperature T; A, *total*; $\Phi = (T_{\alpha=0.99} - T_{\alpha=0.01})/\Delta t$ = heating rate; t = time; $\alpha = m/M$, or a/A = degree of conversion.

experimental runs, 29 thermal analysis runs were selected. The experimental conditions, as well as characteristic parameters for these runs, are listed in Table 2.

In the case of all investigated compounds the above mentioned variables can change the characteristic parameters describing the thermolysis course. The peak temperatures on DTA and DTG, as well as the temperatures at the beginning and the end of decomposition, were shifted toward higher values with increasing weight samples and heating rates. This effect can be clearly seen for the decomposition of Cs_2PbCl_6, but is less distinct in the case of thermolyses of both other hexachloroplumbates or dehydration of $CaC_2O_4 \cdot H_2O$.

It is worth noting that similar regularities have been found by Bocanegra and co-workers [46] for the dehydration of calcium oxalate monohydrate.

TABLE 2

The thermal analyses of alkali metal hexachloroplumbates and calcium oxalate monohydrate

Run no.	Substance (thermal process)	Sample wt. (mg)	Sample holders *	Heating rate ** Φ (K min^{-1})	Owen atmosphere ***	Galvanometer sensitivities		
						DTA	DTG	TG (mg)
1	K_2PbCl_6	100	P	5.3	$S(N_2)$	1/5	1/10	20
2	(dissociation)	100	C	5.4	$S(N_2)$	1/5	1/10	20
3		100	PC	5.4	$S(N_2)$	1/5	1/10	20
4		100	PC(C)	3.4	$S(N_2)$	1/5	1/10	20
5		100	PC(C)	5.3	$S(N_2)$	1/5	1/10	20
6		100	PC(C)	7.6	$S(N_2)$	1/5	1/10	20
7		100	PC(C)	11.8	$S(N_2)$	1/5	1/10	20
8	Rb_2PbCl_6	100	P	3.0	$S(N_2)$	1/5	1/10	20
9	(dissociation)	100	P	5.3	$S(N_2)$	1/5	1/10	20
10		100	P	11.2	$S(N_2)$	1/5	1/10	20
11		100	P	11.1	$D(N_2)$	1/5	1/10	20
12		100	P	24.0	$S(N_2)$	1/5	1/10	20
13		150	P	11.2	$S(N_2)$	1/5	1/10	20
14		800	C	1.5	$D(N_2)$	1/5	1/20	100
15		800	C	3.0	$D(N_2)$	1/5	1/20	100
16		800	C	5.5	$D(N_2)$	1/5	1/20	100
17		800	C	11.3	$D(N_2)$	1/5	1/20	100
18	Cs_2PbCl_6	100	P	2.6	$S(N_2)$	1/5	1/10	20
19	(dissociation)	100	P	4.9	$S(N_2)$	1/5	1/10	20
20		100	P	10.7	$S(N_2)$	1/5	1/10	20
21		100	P	14.5	$S(N_2)$	1/5	1/10	20
22		900	C	1.0	$D(N_2)$	1/5	1/20	100
23		900	C	2.9	$D(N_2)$	1/5	1/20	100
24		900	C	5.2	$D(N_2)$	1/5	1/20	100
25		900	C	11.1	$D(N_2)$	1/5	1/20	100
26	$CaC_2O_4 \cdot H_2O$	100	P	2.9	$S(N_2)$	1/5	1/10	20
27	(dehydration)	100	P	5.0	$S(N_2)$	1/5	1/10	20
28		100	P	10.9	$S(N_2)$	1/5	1/10	20
29		100	P	24.4	$S(N_2)$	1/5	1/10	20

* P = platinum plate (see ref. 42, fig. 3e); C = ceramic crucible (see refs. 43 and 44); PC = platinum crucible (see ref. 42, fig. 3d and ref. 45, fig. 5b); PC(C) = platinum crucible covered with a lid (see ref. 45, fig. 5c).

Furthermore, when a relatively small sample (100 mg) was placed in a narrow layer on a platinum plate the temperature decomposition range, ΔT_α, increased with an increase of the heating rate. On the other hand, when a large sample was placed in a ceramic crucible the influence of heating rate on ΔT_α was less significant. The oven atmosphere (static or dynamic) did not affect the results of the analyses.

The values of the characteristic parameters of thermolyses ($T_{m'}$, T_m, $T_{\alpha=0.01}$, $T_{\alpha=0.99}$ and ΔT_α) for hexachloroplumbates can be placed in the following order: $Rb_2PbCl_6 > K_2PbCl_6 \cong Cs_2PbCl_6$. Based on our data it is impos-

Peak temperature in **		Temperature ** [2—4]		
DTA ($T_{m'}$) (K)	DTG (T_m) (K)	$T_{\alpha=0.01}$ (K)	$T_{\alpha=0.99}$ (K)	$\Delta T_\alpha = T_{\alpha=0.99} - T_{\alpha=0.01}$ (K)
486.5	485.0	422	506	84
488.0	487.0	425	513	88
488.0	487.0	429	528	99
479.5	479.5	428	508	80
490.0	489.0	430	525	95
496.5	496.5	426	536	110
503.0		427	537	110
	583.1	485	611	126
	593.5	470	618	148
	610.8	446	631	185
	613.0	453	634	181
624.5	620.0	436	663	227
	615.3	441	636	195
	565.0	427	596	169
580.3	584.2	437	608	171
606.5	603.1	449	619	170
618.1	608.5	458	626	168
462.0	469.9	418	481	63
478.9	480.4	420	493	73
498.1	495.1	421	508	87
505.6	502.0	425	526	101
	516.4	421	523	102
537.6	534.6	425	541	116
554.4	550.8	453	557	104
580.0	570.7	470	583	113
441.0	439.9	365	471	106
446.6	445.2	370	473	103
459.1	456.5	376	486	110
477.8	469.1	390	511	121

** Cf. Fig. 1.

*** D = Dynamic; S = static; (N_2) = nitrogen.

sible to distinguish the parameters for K_2PbCl_6 and Cs_2PbCl_6.

The enthalpies of thermal decomposition estimated by the method of Stepin et al. [18] are listed in Table 3. In the case of the thermolysis of hexachloroplumbates, ΔH_d^0 values depend slightly upon the weight of sample and probably the shape and material of the sample holder. It was then necessary to distinguish two cases. In Table 3 the appropriate mean values are presented. The enthalpy of dehydration of calcium oxalate monohydrate depends on the heating rate. The interpolation formula presented by eqn.

TABLE 3

Heats of thermal reactions

Substance (thermal process)	Run no. (cf. Table 1)	Temp. range (K)	ΔH_d^0($\times 10^{-5}$ J mole^{-1})		
			This work *	From literature (temp. range, K)	Calculated based on standard enthalpy of fusion (298 K)
K_2PbCl_6 (dissociation)	1– 7	450–500	1.56(±0.11)		
Rb_2PbCl_2	8–13	520–620	0.657(±0.041)		0.729 **, 0.784 ***
(dissociation)	14–17	490–600	0.570(±0.014)		
Cs_2PbCl_6	18–21	430–500	1.21(±0.04)		1.356 ***
(dissociation)	22–25	460–560	0.918(±0.081)		
$CaC_2O_4 \cdot H_2O$	26	410–435	1.33	0.732[48]	0.378 **
(dehydration)	27	410–440	1.14	(410–450)	
	28	410–450	0.930	0.754[49]	
	29	415–460	0.805	(500)	

* The standard deviation is given in parentheses.

** Standard enthalpy of fusion ($\times 10^{-5}$ J mole^{-1}) at 298 K:

$\Delta H_f^0[RbCl_{(c)}] = -4.312[47]$; $\Delta H_f^0[CsCl_{(c)}] = -4.337[47]$; $\Delta H_f^0[PbCl_{2(c)}] = -3.597[47]$; $\Delta H_f^0[Cl_{2(g)}] = 0.00[47]$;

$\Delta H_f^0[Rb_2PbCl_{6(c)}] = -12.95[16]$; $\Delta H_f^0[CaC_2O_{4(c)}] = -13.92[47]$; $\Delta H_f^0[H_2O_{(g)}] = -2.422[47]$; $\Delta H_f^0[CaC_2O_4 \cdot H_2O_{(p)}] = -16.72[47]$.

*** Standard enthalpies of fusion ($\times 10^{-5}$ J mole^{-1}) of rubidium and cesium hexachloroplumbates were calculated based on an approximate method described by Brill and co-workers [16]

$\Delta H_f^0[Rb_2PbCl_{6(c)}] = \Delta H_f^0[PbCl_{6(g)}^{2-}] + 2\,\Delta H_{subl}^0[Rb] + 2\,IP[Rb] - U[Rb_2PbCl_6]$

where U is the lattice energy, ΔH_{subl}^0 is the enthalpy of sublimation, and IP is the ionization potential. Values used in the calculation:

$\Delta H_f^0[PbCl_{6(g)}^{2-}] = -9.281[16]$; $\Delta H_{subl}^0[Rb] = 0.817[47]$; $\Delta H_{subl}^0[Cs] = 0.784[47]$; $IP[Rb] = 4.036[47]$; $IP[Cs] = 3.763[47]$;

$U[Rb_2PbCl_6] = 13.43[7]$; $U[Cs_2PbCl_6] = 13.44[7]$.

(13) was applied to the experimental data

$$\Delta H_d^0 = (\Delta H_d^0)_{\Phi=\infty} + \frac{(\Delta H_d^0)_{\Phi=0} \cdot b_{\Delta H}}{b_{\Delta H} + \Phi} \tag{13}$$

where $(\Delta H_d^0)_{\Phi=\infty}$ and $(\Delta H_d^0)_{\Phi=0}$ are enthalpy of dehydration at $\Phi = \infty$ and $\Phi = 0$, respectively; $b_{\Delta H}$ is constant.

The calculated values of the parameters are: $(\Delta H_d^0)_{\Phi=\infty} = 0.685 \times 10^5$ J mole^{-1}, $(\Delta H_d^0)_{\Phi=0} = 1.64 \times 10^5$ J mole^{-1} and $b_{\Delta H} = 1.92$ K min^{-1}.

It was possible to compare our experimental values with those reported by other authors. For the dissociation of hexachloroplumbates no such data were available. However, the calculated enthalpies of dissociation for Rb_2PbCl_6 and Cs_2PbCl_6, based on standard enthalpy of formation of reactants, are in good agreement with those estimated by us (see Table 3). In the case of $CaC_2O_4 \cdot H_2O$ reported by Beech [48] (DSC method) and Sharma and co-workers [49] (DTA method), the enthalpies of dehydration are in good agreement with our data, while the enthalpy of dehydration calculated based on standard enthalpy of formation of reactants is at least three times lower in comparison with our experimental values.

The kinetic parameters, estimated by previously mentioned methods, for the thermolysis of rubidium hexachloroplumbate are listed in Table 4. Analogous calculations were carried out for other thermoanalytical runs described in Table 2. From these results we expected to obtain valuable information about the nature of thermal processes. In searching for a mechanism of the thermal processes, it is necessary to establish the rules for choosing the function f(α) which describes the experimental results most satisfactorily.

(i) The correlation coefficient, which is very often used for such purposes, did not give us the exact answer. By examination of the data in Table 4 it may be seen that the correlation coefficients for some of the functions f(α) reach high values.

The following were used as further criteria:

(ii) The relative differences of apparent activation energy (ΔE) and Z constant (ΔZ) obtained by four earlier mentioned methods. If several of the functions f(α) had the same correlation coefficients, we assumed that these functions best described the kinetics of the thermal process for which ΔE and subsequently ΔZ values were lower. Such an approach seems to be correct, because most of the authors cited herein imply that various calculation techniques should lead to equivalent results [24].

(iii) Intercept from Freeman and Carroll's approach, which should be close to 1.

Based on the above criteria, mechanism R2 seems to describe most satisfactorily the thermal decomposition of Rb_2PbCl_6 (Table 4). In the same way the choice of the best equation f(α) has been made in the case of other experimental runs. The kinetic parameters for the decomposition of alkali metal hexachloroplumbates depend slightly on sample weight and on the shape and probably the material of the sample holder. It was necessary to distinguish two cases, as was done for the enthalpy of dissociation. The appropriate mean values are listed in Table 5. Using the above criteria we

TABLE 4

Kinetic parameters for the dissociation of Rb_2PbCl_6 (cf. Table 2, Run No. 17 and Fig. 1)

Mechanism (cf. Table 1)	Methods for linearization of kinetic eqn. (3)									
	Freeman and Carroll $[\Delta \ln(d\alpha/dT)]/[\Delta \ln f(\alpha)] = f\{\Delta(1/T)/[\Delta \ln f(\alpha)]\}$				Coats and Redfern					
					$\ln[g(\alpha)/T^2] = f(1/T)$			$\ln\{[g(\alpha)/T^2]/(1-2RT/E)\} = f(1/T)$		
	E *	Z **	r ***	Intercept	E *	Z **	r ***	E *	Z **	r ***
R1					0.475	1.7×10^{3}	0.9998	0.486	2.7×10^{3}	0.9998
R2	0.561	1.5×10^{2}	0.9993	0.452	0.550	5.3×10^{3}	0.9991	0.559	8.0×10^{3}	0.9991
R3	0.561	1.3×10^{2}	0.9993	0.339	0.577	6.9×10^{3}	0.9983	0.585	1.0×10^{4}	0.9983
P1	−1.34	5.2×10^{-15}	0.4131	0.774	0.333	7.5×10	0.9997	0.350	1.5×10^{2}	0.9998
P2	−1.34	4.7×10^{-15}	0.4131	1.03	0.286	2.6×10	0.9997	0.306	6.1×10	0.9998
P3	−1.34	3.7×10^{-15}	0.4131	1.54	0.191	2.7	0.9996	0.224	1.1×10	0.9998
E1	−1.34	8.5×10^{-15}	0.4131	3.09						
B1	0.425	5.5×10	0.9999	0.224						
P4	−1.34	4.8×10^{-15}	0.4131	2.32	0.0487	4.4×10^{-2}	0.9977			
F1	0.561	6.3×10^{2}	0.9993	0.226	0.634	8.5×10^{4}	0.9960	0.642	1.2×10^{5}	0.9961
A2	0.488	6.1×10	0.9998	0.327	0.270	2.4×10	0.9949	0.292	6.1×10	0.9952
A3	0.433	1.3×10	1.000	0.358	0.149	1.1	0.9930	0.193	7.4	0.9945
D1	−1.34	1.0×10^{-14}	0.4131	−3.09	1.04	2.2×10^{8}	0.9998	1.05	2.7×10^{8}	0.9998
D2	0.906	2.0×10^{5}	0.9970	0.589	1.14	1.0×10^{9}	0.9997	1.14	1.2×10^{9}	0.9997
D3	0.665	1.3×10^{3}	0.9988	0.182	1.25	3.1×10^{9}	0.9985	1.25	3.6×10^{9}	0.9985
D4	0.792	6.0×10^{3}	0.9979	0.398	1.17	5.5×10^{8}	0.9994	1.18	6.5×10^{8}	0.9994

TABLE 4 (*continued*)

Mechanism (cf. Table 1)	Methods for linearization of kinetic eqn. (3)					
	Gorbachev $\ln\{[g(\alpha)/T](E/RT+2)\} = f(1/T)$			Horowitz and Metzger $\ln[g(\alpha)] = f(\theta)$		
	E *	Z **	r ***	E *	Z **	r ***
R1	0.483	2.4×10^3	0.9998	0.662	9.7×10^4	0.9989
R2	0.556	7.3×10^3	0.9991	0.750	4.0×10^5	0.9999
R3	0.583	9.4×10^3	0.9983	0.781	5.7×10^5	0.9999
P1	0.343	1.2×10^2	0.9998	0.496	2.9×10^3	0.9989
P2	0.297	4.4×10	0.9997	0.441	8.8×10^2	0.9989
P3	0.205	5.9	0.9997	0.331	7.7×10	0.9989
E1						
B1						
P4	0.0748	2.7×10^{-1}	0.9993	0.165	1.5	0.9989
F1	0.640	1.1×10^5	0.9960	0.849	8.5×10^6	0.9991
A2	0.282	4.3×10	0.9951	0.424	8.2×10^2	0.9991
A3	0.166	2.8	0.9940	0.283	3.1×10	0.9991
D1	1.05	2.6×10^8	0.9998	1.32	7.7×10^{10}	0.9989
D2	1.14	1.2×10^9	0.9997	1.43	5.0×10^{11}	0.9998
D3	1.25	3.7×10^9	0.9985	1.56	2.2×10^{12}	0.9999
D4	1.18	6.4×10^8	0.9994	1.48	3.0×10^{11}	0.9999

* Activation energy ($\times 10^{-5}$ J mole^{-1}).

** Constant (s^{-1}).

*** Correlation coefficient.

TABLE 5

Kinetic parameters for the thermolysis of alkali metal hexachloroplumbates *

Substance	Run no. (cf. Table 2)	Mechanism (cf. Table 1)	Methods of treatment		
			Freeman and Carroll		
			E ($\times 10^{-5}$ J mole^{-1})	Z (s^{-1})	Intercept
K_2PbCl_6	1— 7	R2	2.42(±0.12)		1.3(±0.6)
		F1	2.42(±0.12)		0.65(±0.28)
Rb_2PbCl_6	8—13	R2	0.543(±0.110)	1.2×10^2	0.48(±0.26)
		F1	0.543(±0.110)	4.5×10^2	0.24(±0.13)
		D2	0.958(±0.079)	1.4×10^6	0.58(±0.10)
	14—17	R2	0.599(±0.066)	1.0×10^3	0.53(±0.28)
		F1	0.599(±0.066)	4.6×10^3	0.26(±0.14)
		D2	1.01(±0.36)	4.7×10^9	0.71(±0.51)
Cs_2PbCl_6	18—21	R2	1.30(±0.04)	5.3×10^{11}	1.2(±0.2)
		F1	1.30(±0.04)	1.6×10^{12}	0.59(±0.11)
		D3	2.01(±0.17)	1.9×10^{20}	0.56(±0.12)
	22—25	R2	0.929(±0.023)	1.3×10^6	0.62(±0.13)
		F1	0.929(±0.023)	4.8×10^6	0.31(±0.07)
		D2	1.75(±0.05)	1.8×10^{14}	1.1(±0.4)

* The standard deviation is given in parentheses.

met with some difficulties; however, if was necessary to find the best function f(α) based on a few experimental runs for certain compounds. Such cases, which are not easily distinguishable among the others, are subsequently listed in Table 5.

Kinetic parameters calculated based on Coats and Redfern's approach [eqn. (9)] and Gorbachev's method [eqn. (12)] did not vary significantly from those estimated using the equation

$$\ln[g(\alpha)/T^2] = f(1/T)$$

as may be seen in Table 4. The differences between E and Z values obtained from several experimental runs were usually larger than those resulting from application of more accurate interpolation procedures. Thus, Table 5 does not contain values of kinetic parameters estimated based on eqns. (9) and (12).

It is interesting to compare the values of apparent activation energy and Z constant for the thermolyses of hexachloroplumbates. For certain mechanisms of decomposition they decrease in the order: $K_2PbCl_6 > Cs_2PbCl_6 > Rb_2PbCl_6$. Analogous relations may be seen for evaluated enthalpies of dissociation. It is worth noting that the values of the enthalpies of dissociation are similar to appropriate values of the apparent activation energies in the case of the R2 mechanism.

Based on the assumed criteria, functions f(α), which describe most satisfactorily the dehydration of calcium oxalate monohydrate, have been

Coats and Redfern		Horowitz and Metzger	
E ($\times 10^{-5}$ J mole^{-1})	Z (s^{-1})	E ($\times 10^{-5}$ J mole^{-1})	Z (s^{-1})
1.65(±0.18)	4.5×10^{18}	1.83(±0.15)	1.1×10^{21}
1.88(±0.21)	7.4×10^{21}	2.07(±0.21)	1.0×10^{24}
0.635(±0.043)	3.5×10^{3}	0.808(±0.047)	1.5×10^{6}
0.741(±0.050)	9.3×10^{5}	0.926(±0.054)	5.2×10^{7}
1.30(±0.08)	4.7×10^{10}	1.54(±0.09)	8.4×10^{12}
0.557(±0.026)	4.4×10^{3}	0.757(±0.026)	3.4×10^{5}
0.623(±0.033)	9.7×10^{4}	0.871(±0.034)	1.1×10^{7}
1.15(±0.05)	1.4×10^{9}	1.44(±0.05)	7.2×10^{11}
1.21(±0.05)	3.7×10^{12}	1.40(±0.06)	3.7×10^{14}
1.35(±0.04)	4.4×10^{14}	1.52(±0.06)	6.2×10^{16}
2.58(±0.09)	1.5×10^{28}	2.82(±0.12)	3.2×10^{31}
0.909(±0.071)	9.1×10^{7}	1.11(±0.06)	8.2×10^{9}
1.05(±0.08)	5.9×10^{9}	1.27(±0.07)	8.4×10^{11}
1.81(±0.15)	2.4×10^{17}	2.12(±0.13)	1.8×10^{20}

chosen. The kinetic parameters obtained for these functions are listed in Table 6. It may be seen that in all cases E and Z values vary with the heating rate. Similar dependences have been found by Nair and Ninan [39,50,51] for the dehydration of $CaC_2O_4 \cdot H_2O$, who have suggested, however, mechanism R3 as the rate-determining process. From our data four functions f(α) describe equally well the dehydration process. For describing the dependences of apparent activation energy and Z factor on temperature, two equations may be proposed, by analogy to eqn. (13)

$$E = E_\infty + \frac{E_0 b_E}{b_E + \Phi} \tag{14}$$

$$\ln Z = \ln Z_\infty + \frac{\ln Z_0 \cdot b_Z}{b_Z + \Phi} \tag{15}$$

where E_∞, Z_∞ and E_0, Z_0 represent apparent activation energies and Z factor values at $\Phi = \infty$ and $\Phi = 0$, respectively; b_E and b_Z are constants.

Equations (14) and (15) describe our experimental results better than those proposed by Nair and Ninan [39,50,51]: $E = \mathrm{f}(1/\Phi)$ and $\ln Z = \mathrm{f}(1/\Phi)$. In our opinion these equations also seem to be more realistic, because they consider the existence of finite values of the kinetic parameters at $\Phi = 0$.

The data presented in Table 6 are in good agreement with those published by other authors [39,50—52] for the dehydration of calcium oxalate monohydrate.

TABLE 6

Kinetic parameters for the dehydration of calcium oxalate monohydrate

Mechanism (cf. Table 1)	Run no. (cf. Table 2)	Methods of treatment							
		Freeman and Carroll		Coats and Redfern				Horowitz and Metzger	
		Activation energy *	Z factor **	Activation energy *		Z factor **		Activation energy *	Z factor **
		E	Z	E	E_∞ E_0 b_E	Z	Z_∞ Z_0 b_Z	E	Z
R3	26	1.17	1.1×10^{11}	1.51	0.741 75.2 0.03	1.2×10^{17}	4.9×10^{7} ∞ 0.03	1.69	1.8×10^{19}
	27	0.880	4.6×10^{7}	1.16		6.0×10^{12}		1.31	4.4×10^{14}
	28	0.755	1.4×10^{6}	0.962		2.5×10^{10}		1.11	1.4×10^{12}
	29	0.700	3.3×10^{5}	0.836		6.9×10^{8}		1.01	7.8×10^{10}
F1	26	1.17	5.5×10^{11}	1.65	0.800 14.8 0.18	2.1×10^{19}	5.7×10^{8} 1.6×10^{75} 0.48	1.84	4.4×10^{21}
	27	0.880	2.4×10^{8}	1.29		1.0×10^{15}		1.46	9.8×10^{16}
	28	0.755	6.5×10^{6}	1.07		2.0×10^{12}		1.23	1.4×10^{14}
	29	0.700	1.6×10^{6}	0.889		1.0×10^{10}		1.07	1.4×10^{12}
A2	26	0.788	6.4×10^{8}	0.790	0.361 5.68 0.24	4.5×10^{8}	5.9×10^{3} ∞ 0.12	0.921	1.9×10^{10}
	27	0.609	6.2×10^{4}	0.611		3.6×10^{6}		0.729	1.0×10^{8}
	28	0.514	4.9×10^{3}	0.500		2.1×10^{5}		0.615	5.3×10^{6}
	29	0.360	1.1×10^{2}	0.408		1.9×10^{4}		0.534	7.0×10^{5}
A3	26	0.584	1.5×10^{4}	0.503	0.216 3.80 0.24	1.0×10^{5}	8.9×10 ∞ 0.06	0.614	2.6×10^{6}
	27	0.500	2.0×10^{3}	0.383		4.4×10^{3}		0.486	8.9×10^{4}
	28	0.427	3.1×10^{2}	0.309		7.7×10^{2}		0.410	1.5×10^{4}
	29	0.245	3.6	0.247		1.9×10^{2}		0.357	4.7×10^{3}

* E_∞, E_0, b_E from eqn. (14); E, E_∞, E_0($\times 10^{-5}$ J mole^{-1}); b_E(K min^{-1}).

** Z_∞, Z_0, b_Z from eqn. (15); Z, Z_∞, Z_0(s^{-1}); b_Z(K min^{-1}).

DISCUSSION

The thermal analysis data indicate that the thermolyses of alkali metal hexachloroplumbates are one-step processes accompanied by the loss of chlorine to the gas phase, probably as Cl_2. The composition and structure of the solid products of the thermolyses have not been studied. It is well known that alkali metal chlorides or $PbCl_2$ do not undergo any structural transformation [53—55] or melting [47,56] in the temperature range 300—700 K. To our knowledge, no information indicating the possibility of formation of any molecular complexes between alkali metal halides and lead chloride in the temperature range 300—700 K are available. This was supported by thermal analysis data obtained for mixtures of appropriate alkali metal halides and lead chloride at a molar ratio of 2 : 1. No thermal effect was found upon heating such mixtures up to 700 K. Molecular complexes of alkali metal halides and $PbCl_2$ have been identified, however, in the gas phase [57—59] and in condensed phases [60—63] on heating the appropriate systems above their melting temperatures. Thus, it seems less probable that formation of such compounds occurs simultaneously with the destruction of the crystal lattice of hexachloroplumbates upon heating. Based on the above consideration we assume that the thermolyses of alkali metal hexachloroplumbates result in the formation of the appropriate alkali metal halides and lead chloride in the solid state. In order to describe the thermal processes the following equation may be proposed

$$M_2(I)PbCl_{6(s)} \rightarrow 2\,M(I)Cl_{(s)} + PbCl_{2(s)} + Cl_{2(g)} \qquad (16)$$

where $M(I)$ = K, Rb, Cs.

The kinetic information obtained for the decomposition of alkali metal hexachloroplumbates indicates that thermal processes are controlled mainly by phase boundary reaction of cylindrical symmetry. The best linear correlation, and the best agreement of kinetic parameters evaluated by several methods, were found in the case of the R2 mechanism. This conclusion seems to be supported also by thermodynamic estimation. Data in Table 3 indicate a good agreement between experimental and literature values. This means that the approach of Stepin et al. [18] was correctly applied. As mentioned before, this method may be applied for phase boundary reactions.

The enthalpies of dissociation for hexachloroplumbates have values that are very close to the appropriate apparent activation energies for the R2 mechanism, which may indicate that the back reaction of (16) takes place with a very low activation barrier. This process cannot be realized in the heterogeneous system. However, it is well known that alkali metal hexachloroplumbates may be easily synthesized by saturating with chlorine a suspension of $PbCl_2$ in aqueous solutions of alkali metal halides [1].

Based on kinetic considerations, the activation energy of the decomposition process should be higher than the enthalpy of dissociation. Among the possible pathways for thermolysis, the one requiring less excess of energy over ΔH_d^0 seems to be more probable. In the case of the decomposition of hexachloroplumbates, this corresponds to the R2 mechanism.

Similar considerations lead to the conclusion that in the case of the dehydration of $CaC_2O_4 \cdot H_2O$, mechanism R3 may be the rate-determining process. This is in agreement with the suggestion of Nair and Ninan [39,50, 51].

Examination of the courses of the thermal decomposition of alkali metal hexachloroplumbates, based on characteristic parameters of thermolysis, namely, $T_{\alpha=0.01}$, T_m, $T_{m'}$, leads to the conclusion that Rb_2PbCl_6 has the highest thermal stability and that K_2PbCl_6 and Cs_2PbCl_6 have fairly equal thermal stabilities. It is worth noting that similar regularities have been found in the case of the thermolysis of $M_2(I)IrCl_6$ [64]. However, for most compounds of the type $M_2(I)M(IV)X_6$ (for example, M(IV) = Te, X = Cl [65]; M(IV) = Pt, X = Cl [66]; M(IV) = Tc, X = Br [67]) the values of the characteristic parameters of thermolyses increase with increases in the thermochemical radii of the alkali metal cations.

The kinetic and thermodynamic parameters of the thermolyses indicate K_2PbCl_6 as the most stable compound among the alkali metal hexachloroplumbates. This anomaly may arise from the different crystal structure of K_2PbCl_6 as compared with Rb_2PbCl_6 or Cs_2PbCl_6. Potassium hexachloroplumbate has a monoclinic structure [5—7] and undergoes transformation at 333 K to a cubic structure, the latter being characteristic of both the other hexachloroplumbates at room temperature [6,7]. Experimental data for K_2PbCl_6 did not show a peak on the DTA curve near the temperature corresponding to crystal structure transformation. This may indicate that K_2PbCl_6 maintains its crystal lattice structure upon heating to the beginning of decomposition.

Another, more probable explanation of the relatively high values of the kinetic and thermodynamic parameters for the thermolysis of K_2PbCl_6 may arise from the abnormal course of its thermal decomposition process. The crystals of this compound, even when ground to smaller dimensions, rapidly shattered just before the onset of decomposition. In some experimental runs this necessitated covering the crucible with a lid which prevented the loss of samples (Table 2). This effect could introduce systematic error to the kinetic and thermodynamic calculations, because TG and DTG curves were recorded for "superheated" samples.

It is worth noting that in the case of alkali metal hexachlorotellurates, which have similar structural features to hexachloroplumbates [6], the enthalpy of dissociation [68], as well as the characteristic parameters of thermolyses [65], show typical relations with the thermochemical radii of the cations. However, during the thermolysis of Rb_2TeCl_6 effects similar to those for K_2PbCl_6 thermolysis have been observed [65].

Investigation of reaction kinetics in the solid state is not easy. Generally, the use of one particular method, among widely recommended non-isothermal methods, is not sufficient to find the reaction mechanism. In this work we have tried to apply simultaneously four well-known methods, which we have proposed to extend to a larger number of f(α) functions. This allowed us to restrict the number of possible reaction mechanisms. We decided to apply such an approach in spite of the fact that it was recently criticized by Arkhangel'skii et al. [69]. In our opinion, results presented by these authors seem to be inadequate on some points.

Comparison of the kinetic and thermodynamic parameters of the thermolyses may be helpful in searching for a reaction mechanism.

Results of calculations listed in Table 4, as well as considerations presented earlier, made possible a comparison of four applied methods of linearization of eqn. (3). Based on purely mathematical points of view, eqn. (12) is the most accurate because two terms from Schlömilch's approximation have been considered during its derivation [37]. However, comparison of results in Tables 4 and 5 leads to the conclusion that Coats and Redfern's method using the form $g(\alpha)/T^2 = f(1/T)$ is the simplest and accurate enough approximation procedure for use in kinetic calculations. Using Horowitz and Metzger's method, values of kinetic parameters higher than those in the case of Coats and Redfern's method were obtained. Also Horowitz and Metzger's approach seems to be the least accurate integral method among those applied by us, because of the numerous simplifications introduced during derivation of eqn. (11). Freeman and Carroll's method cannot be recommended by us for sole use in searching for the reaction mechanism; however, this approach may be helpful when used together with integral methods.

ACKNOWLEDGEMENT

The authors would like to thank Mrs. A. Rymkiewicz for experimental assistance.

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