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THERMAL REACTIONS OF LEAD(IV) CHLORIDE COMPLEXES IN THE SOLID STATE. PART VI. THERMAL PROPERTIES, THERMOCHEMISTRY AND KINETICS OF THE THERMAL DECOMPOSITION OF ALKANAMINIUM HEXACHLOROPLUMBATES *

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ABSTRACT

Thermal properties of unbranched compounds of general formula $[(C_nH_{2n+1})_pNH_{4-p}]_2$ $PbCl_6$, with $n = 1$–4 and $p = 2$–4, and several other cyclic and open chain branched aliphatic alkanaminium hexachloroplumbates were examined by thermoanalytical methods (DTA, TG, and DTG). Complementary information was gathered by performing thermolyses in an apparatus enabling quantitative determination of evolved chlorine. Thermal decomposition of the compounds studied takes place in two stages:
(i) liberation of chlorine

$$(R_pNH_{4-p})_2PbCl_{6(c)} \rightarrow Cl_{2(g)} + \left[PbCl_2 + 2(R_pNH_{4-p})Cl\right]_{(s)}$$

(ii) volatilization of amine hydrochlorides ($a = 0$) or decomposition of quaternary salts ($a = 1$)

$$\left[PbCl_2 + 2(R_pNH_{4-p})Cl\right]_{(s)} \rightarrow PbCl_{2(c)} + 2R_{p-a}NH_{3-p+a(g)} + 2(1-a)HCl_{(g)} + 2aRCl_{(g)}$$

Amounts of chlorine evolved were usually less than stoichiometric as some was consumed in secondary processes.

For compounds with well-defined decomposition steps the thermodynamics and kinetics of the first stage were examined. The crystal lattice energies of the compounds were estimated using the Kapustinskii–Yatsimirskii equation. Derived values, together with those available from the literature, were used for the estimation of the enthalpy of formation and enthalpy changes for the first step of the thermal decomposition of the salts. The kinetics of the thermal decomposition were analysed by considering two different forms of kinetic equation, i.e. the "classical" form and that based on an assumption: $\alpha = f(t, T)$. No substantial differences between kinetic parameters derived by these methods were found. Some aspects of this problem are discussed, particularly with regard to the existing controversy over the adequate form of kinetic equations under non-isothermal conditions.

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* Presented in part at the 8th International Conference on Thermal Analysis, Bratislava, Czechoslovakia, August 1985 [1].

TABLE 1

The thermal analysis of alkanaminium hexachloroplumbates

Substance [a]		Experimental conditions [b]	Weight loss (%)			Peak temperature [d] (K)				Temperature [d] (K)			
No.	Formula		Thermal process [c]	Experimental, from TG	Theoretical	DTG [c]	DTA			$T_{0.01}$ [f]	$T_{0.1}$ [g]	$T_{0.9}$ [g]	ΔT
							T_σ	T_m	T_p [c]				
1	$(Me_2NH_2)_2PbCl_6$	A	D		13.8	420m			421w	370			
			$(D+V)_U$	45.5	45.7	431m,sh			433w				
						487w			487w				
						535s,b			537m				
2	$(Me_3NH)_2PbCl_6$	A	D		13.1	461s,sh		445	458w	390			
						488m			490w				
			$(D+V)_U$	48	48.5	523s,b			527w				
3	$(Me_4N)_2PbCl_6$	A	D		12.5	483m,b			485w,b	440			
						511w							
			$(D+V)_U$	51	51.1	551w							
						571m			575w				
						602m			605w				
						673s,sh			678w				
4	$(Et_2NH_2)_2PbCl_6$	A	D		12.5	398m			403m	375			
						413w							
			$(D+V)_U$	51	51.1	521s,b			521m				
5	$(Et_3NH)_2PbCl_6$	A	D		11.4	387w		372	381w	370			
						423w							
			$(D+V)_U$	55	55.5	509s,b			507m,b				
6	$(Et_4N)_2PbCl_6$	A	D		10.4	497s,sh		353	500m	480			
						506m							
			$(D+V)_U$	59	59.1	584s,sh			577m				

7	$(n\text{-Pr}_2NH_2)_2PbCl_6$	A	D	11.5	11.4	401m			403w	370	378.4	404.9	26.5
						507s			508m				
			D + V	55	55.5	558m			560w				
8	$(n\text{-Pr}_3NH)_2PbCl_6$	A	D		10.0	391w,sh		347	393w	370			
						402w							
			$(D + V)_U$	61	60.7	418w							
						476s			476m				
						565s			563m,b				
9	$(n\text{-Pr}_4N)_2PbCl_6$	A	D		8.9	468w,sh		414	461w	430			
						504m			504w				
			$(D + V)_U$	65	64.9	549s			549m				
10	$(i\text{-PrNH}_3)_2PbCl_6$	A	D	13	13.1	423m			424w	380	397.1	437.8	40.7
						528s			530m				
			D + V	49	48.5								
11	$(i\text{-Pr}_2NH_2)_2PbCl_6$	A	D		11.4	421s,sh			423w	370			
									441w				
			$(D + V)_U$	56	55.5	510s			512m				
12	$(n\text{-Bu}_2NH_2)_2PbCl_6$	A	D		10.4	365m			365w	350			
									475w				
			$(D + V)_U$	59	59.1	509s			512m				
						581s			585m				
13	$(n\text{-Bu}_3NH)_2PbCl_6$	A	D		8.9	420w,sh		376	422w	365			
						484s			486m				
			$(D + V)_U$	64	64.9	545s			546m				
14	$(n\text{-Bu}_4N)_2PbCl_6$	A	D		7.8	456w	373	424	456w (exo)	430			
			$(D + V)_U$	69	69.3	483s			482m				
						539s			541m				

TABLE 1 (Continued)

Substance [a]		Experimental conditions [b]	Weight loss (%)			Peak temperature [d] (K)				Temperature [d] (K)			
No.	Formula		Thermal process [c]	Experimental, from TG	Theoretical	DTG [e]	DTA			$T_{0.01}$ [f]	$T_{0.1}$ [g]	$T_{0.9}$ [g]	ΔT
							T_σ	T_m	T_p [e]				
15	$(i\text{-BuNH}_3)_2\text{PbCl}_6$	A	D	12	12.5	386m			391w	340	352.9	395.6	42.7
						535s			535m				
			D+V	51	51.1								
16	$(s\text{-BuNH}_3)_2\text{PbCl}_6$	A	D		12.5	412m,sh			414m	370			
									470w				
			$(D+V)_U$	51	51.1	504m			504m				
						564m			565w				
17	$(t\text{-BuNH}_3)_2\text{PbCl}_6$	A	D		12.5	401w			402m	470			
						423w			426w				
			$(D+V)_U$	51	51.1	512m			512m				
						556w			561m				
18	$(i\text{-Bu}_2\text{NH}_2)_2\text{PbCl}_6$	A	D		10.4	389m			392m	345			
									458w				
			$(D+V)_U$	59	59.1	475m			477w				
						579s,sh			579m				
19	$(i\text{-PentNH}_3)_2\text{PbCl}_6$	A	D	12	11.9	393m			396w	360	372.9	399.1	26.2
						546s			548m				
			D+V	54	53.4								
20	$(c\text{-HexNH}_3)_2\text{PbCl}_6$	A	D	11.5	11.4	404m			405w	355	370.1	410.5	40.4
						547s			549m				
			D+V	55	55.2								
21	$(\text{Pyr}\cdot\text{H})_2\text{PbCl}_6$	A	D		12.6	400m			405w	365			
									542w				

			$(D+V)_U$	50.5	50.7	570s	567m				
		B	D		12.6	410m	412m 580m,sh	365			
			$(D+V)_U$	48.5	50.7	632m,b	641s,b				
22	$(Pip\cdot H)_2PbCl_6$	A	D	12	12.0	422m 515w	420w 517w	370	385.5	425.7	40.2
			$(D+V)_U$	53	53.0	560s	561s				
23	$(Quin\cdot H)_2PbCl_6$	A	D		11.0	452w 468m	456w (exo) 470w	410			
			$(D+V)_U$	57	56.8	520m 539w 600s	523w 544w 667m(exo)				
		B	D		11.0	446w	452m (exo)	420			
			$(D+V)_U$	57	56.8	468m 522m 623m 676w,b	525s,b 669s (exo)				

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[a] For names of amines see ref. 11, Table 2.

[b] A, mass of sample = 80 mg, sensitivities of DTG, DTA, and TG galvanometers equal to 1/10, 1/5 or 1/3, and 50 mg, respectively. B, mass of sample = 300 mg, sensitivities of DTG, DTA, and TG galvanometers equal to 1/10, 1/3, and 200 mg, respectively.

[c] D = decomposition step which corresponds to reaction (3); V = volatilization step which refers to reaction (4). Subscript U denotes unresolved reaction stages.

[d] The symbols were taken from ref. 12. T_p = temperature of the peak, T_σ = temperature of a solid-state phase transition, T_m = temperature of melting, and T_α = temperature at which the degree of conversion is equal to α (i.e. $T_{0.1} = T_{\alpha=0.1}$).

[e] w = weak, m = medium, s = strong, sh = sharp, and b = broad.

[f] $T_{0.01}$ = decomposition temperature regarding both reaction stages.

[g] Temperatures correspond to the first decomposition step: $T_{0.1}$ = temperature of the onset of a decomposition; $T_{0.9}$ = temperature at the end of a reaction; $\Delta T = T_{0.9} - T_{0.1}$, is the temperature interval for a decomposition.

INTRODUCTION

Solid derivatives of hexachloroplumbic acid are interesting model compounds for the investigation of properties of hexachlorometallates of the main group IV elements owing to the unique behaviour of the central atom [2,3]. These compounds may be considered as molecular complexes of $PbCl_4$ and appropriate chloride salts or other donors (e.g. chloroalkanes). Lead tetrachloride is thermodynamically unstable and this feature is due to the relatively high Pb^{4+}/Pb^{2+} potential (+1.5 V [4]) compared with that of $Cl_2/2Cl^-$ (+1.36 V [5]). Molecular complexes of $PbCl_4$ can exist, however, because the compound exhibits relatively strong electron-acceptor properties. Thermal stability of hexachloroplumbates, i.e. derivatives originating from $PbCl_6^{2-}$, is limited and depends markedly on the structure of cations forming appropriate salts. Hexachloroplumbates of various salts have been examined in the past [6] and this work is a continuation of the cycle. The choice of alkanaminium cations for the study creates an opportunity for examining the influence of the size and structure of the cation on thermal features of hexachloroplumbates in a relatively wide range. On the other hand, these derivatives are relatively simple as model compounds for the investigation. A further aim of this work is to provide basic thermochemical characteristics for alkanaminium hexachloroplumbates. Such data are of interest since they can provide important information on the thermal behaviour of the compounds of this group. These characteristics are not available for the majority of hexachloroplumbates studied. We also intend to examine some aspects of the kinetics of the thermal decomposition of some of the compounds studied, particularly in relation to the application of various kinetic methods and computational procedures.

EXPERIMENTAL

All reagents used were the best available grades. Hexachloroplumbic acid and its alkanaminium salts were prepared by reported methods [2,6,7]. The synthesized salts were analysed for Pb(II) and Pb(IV). Compounds more than 96% pure, with respect to Pb(IV) content, were always used for investigations.

The thermal analyses were performed on an OD-103 derivatograph (Monicon) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen. The sample was placed on one of the platinum plates (ref. 8, Appendix 1, No. 4). Other operating conditions are described in Table 1.

The isothermal experiments were carried out by the procedure described previously [9]. Details of analytical methods used have also been reported elsewhere [9].

TABLE 2

α versus T dependencies for the first stage of the thermal decomposition of hexachloroplumbates

α	T (K)					
	Substance No. [a]					
	7	10	15	19	20	22
0.1	378.4	397.1	352.9	372.9	370.1	385.5
0.2	386.8	405.8	363.2	379.5	381.7	397.4
0.3	392.0	412.3	370.6	383.8	388.6	405.1
0.4	395.0	417.3	375.4	386.6	393.5	411.2
0.5	397.3	421.6	379.4	389.5	397.7	414.9
0.6	399.8	425.7	383.4	391.8	401.4	418.2
0.7	401.9	429.4	386.8	393.8	403.7	420.9
0.8	403.3	433.4	390.5	396.1	406.6	423.2
0.9	404.9	437.8	395.6	399.1	410.5	425.7

[a] For information see Table 1.

In the case of compounds showing well-defined reaction stages the experimental TG curves were used for the examination of thermodynamics and kinetics of the first step of thermolysis. The temperature (T) values corresponding to certain values of the extent of reaction (α) were determined as previously described [6,10]. Each α vs. T data point used for the calculations was obtained from at least three replicate measurements. This information is compiled in Table 2.

RESULTS AND DISCUSSION

1. General features of the thermal decomposition

All alkanaminium hexachloroplumbates studied undergo decomposition upon heating to 700 K. Thermal analyses of four compounds chosen as examples are shown in Figs. 1 and 2, and the results of thermoanalytical investigations of all the compounds examined are compiled in Table 1.

Thermal decomposition of 3-methyl-1-butanaminium hexachloroplumbate (Fig. 1A) presents the simplest reaction pattern. In the first step of its thermolysis one molecule of Cl_2 from one molecule of hexachloroplumbate is released. As a result of this process a mixture of $PbCl_2$ and 2 molecules of $[(CH_3)_2CHCH_2CH_2NH_3]Cl$ is formed from which the latter compound volatilizes in the second stage. The shape of thermoanalytical curves corresponding to the second step is the same as that in the case of volatilization of pure amine hydrochloride [11]. This implies that both components of the mixture occur as separate crystal forms. Several other hexachloroplumbates

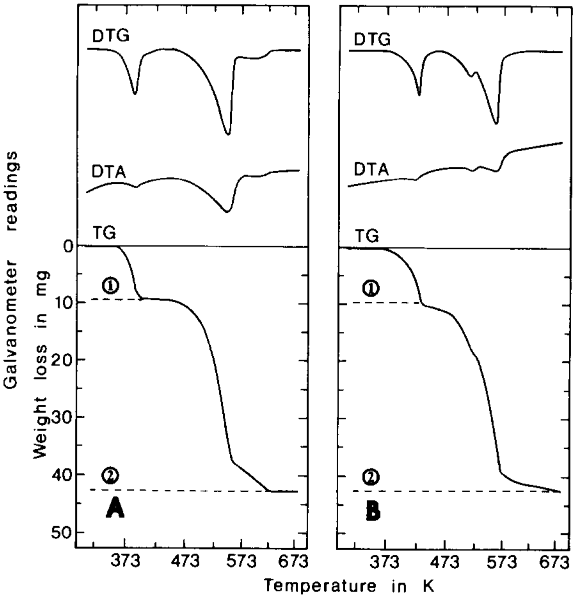

Fig. 1. Thermal analyses of 3-methyl-1-butanaminium hexachloroplumbate (A) and piperidinium hexachloroplumbate (B). The dashed lines indicate the theoretical weight losses in the first (1) and second (2) reaction stage, respectively.

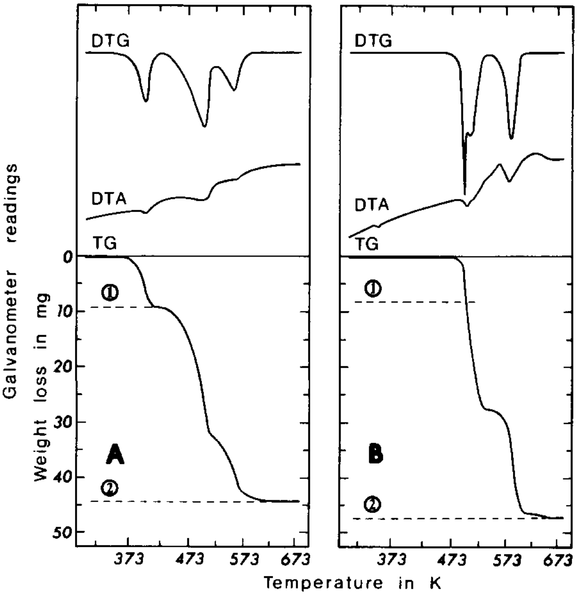

Fig. 2. Thermal analyses of N-propyl-1-propanaminium hexachloroplumbate (A) and N,N,N-triethylethanaminium hexachloroplumbate (B). The dashed lines indicate the theoretical weight losses in the first (1) and second (2) reaction step, respectively.

studied, namely: 2-propanamine, 2-methyl-1-propanamine, and cyclohexanamine, show similar behaviour upon heating (Table 1).

A somewhat different pattern of thermolysis is exhibited by hexachloroplumbates of piperidine and *N*-propyl-1-propanamine. The first step of the thermal decomposition of both these derivatives is identical to that for 3-methyl-1-butanaminium hexachloroplumbate. The second stage is more complex since two peaks are seen in the DTA and DTG curves. Thermoanalytical investigations revealed that $PbCl_2$ undergoes no thermal transformations between room temperature and ~ 690 K [13]. Thus, the observed effects cannot be due to the presence of this compound. On the other hand, pure alkanaminium chlorides, which are expected to be formed in the first stage, should volatilize smoothly as was demonstrated in our previous work [11]. A possible explanation of this phenomenon could be that lead chloride and amine hydrochlorides form complex salts either instantaneously with the decomposition of parent molecules of hexachloroplumbates or upon further heating of the mixture of solid products of the first step. Such species may exhibit different behaviour upon heating to that characteristic of pure $PbCl_2$ or amine hydrochlorides, and thus their presence could complicate the course of thermolysis. The extend of transformation of both reactants into mixed derivatives is presumably the major factor affecting the course of the second stage. The thermoanalytical curves in Fig. 1B indicate that only a minor part of the products of the first step is involved in the formation of mixed salts. On the other hand, upon decomposition of *N*-propyl-1-propanaminium hexachloroplumbate (Fig. 2A) mostly mixed salts are formed. This means that the second stage, corresponding to the decomposition of the latter compound, shows no feature characteristic of the volatilization of pure amine hydrochloride [11].

Mixed salts undoubtedly occur also upon decomposition of other hexachloroplumbates studied. The effects due to their presence are, however, often overshadowed by other processes whose nature will be discussed subsequently.

Interactions between $PbCl_2$ and piperidine or *N*-propyl-1-propanamine hydrochlorides, leading to the formation of mixed salts, have not, so far, been investigated. In our previous work [6] we have shown that some other amine hydrochlorides mixed with $PbCl_2$ (in the ratio 2:1, respectively) exhibit similar behaviour upon heating to that characteristic for the residue from decomposition of appropriate hexachloroplumbates. Further support for this hypothesis comes from the fact that the existence of double salts between $PbCl_2$ and NH_4Cl [14–17] or other hydrochlorides or organic bases (e.g. quinolinium chloride [18]) has been confirmed experimentally. Thermolysis of $(NH_4)_2PbCl_6$ presents a complex pattern also [6], and this behaviour can be mostly ascribed to the formation of double salts with the participation of solid products from the first stage of the process.

Thermal decomposition of the remaining compounds investigated exhibits a more complex nature, but some general regularities can be seen. The total weight loss estimated from TG curves corresponds always, within experimental error, to the formation of $PbCl_2$. The residue was sometimes light-grey in colour which could be due to the contamination of $PbCl_2$ with traces of carbonization products. This indicates that both Cl_2 and appropriate amine hydrochlorides volatilize completely during the thermal decomposition of the compounds studied. As thermoanalytical data show the pathways for the thermal processes are apparently not simple. To obtain further insight into this problem we determined the amounts of chlorine evolved under various experimental conditions. The results, presented in Table 3, indicate that decompositions carried out at temperatures corresponding to the first step always afforded more chlorine than those performed at higher temperatures. The amounts of liberated chlorine decrease with a decrease in the flow rate of the inert gas through the reactor and in the presence of the appropriate amine hydrochlorides. Further, when the compounds studied were covered with a layer of a foreign substance ($PbCl_2$) the values of ν were lower than those obtained in the case of pure substances. A similar effect causes the increase of the mass of the sample. All this evidence shows that some of the chlorine is consumed in secondary processes. Moreover, the results of isothermal investigations indicate that processes leading to the consumption of chlorine occur predominantly in the gaseous phase, and this is borne out by the fact that all factors influencing diffusion of products to the gas phase and their removal from the reaction zone also affect markedly the amounts of evolved chlorine (Table 3). When the reaction stages are clearly separate in the temperature scale, the chlorine liberated in the first step is removed from the reaction zone before the alkanaminium chlorides begin to sublime. This reaction course is actually observed only for the compounds listed in Table 2. Data from isothermal experiments generally confirm this hypothesis although stoichiometric amounts of chlorine have not always been detected upon decomposition of these compounds at low temperatures.

A possible source of this discrepancy may be the experimental conditions which have been chosen arbitrarily to enable a comparison of properties of various compounds upon heating (Table 3).

It is generally recognized that amine hydrochlorides exist in the gaseous phase in the form of dissociated fragments, i.e. amines and HCl [11]. Therefore, only non-protonated alkanamines participate in gas-phase chlorination processes. Such processes primarily lead to the substitution of H atoms, bonded to nitrogen, by chlorine, giving chloramines [19–22], i.e.

$$NH_{3(g)} + 3Cl_{2(g)} \rightarrow NCl_{3(l)} + 3HCl_{(g)} \qquad \Delta H_{298} = -0.8\ \text{kJ mol}^{-1} \qquad (1)$$

The estimated ΔH value from the available literature data [23], for reaction (1), indicates that the process requires only a small thermochemical barrier to be overcome. This barrier should increase when all reactants in the

TABLE 3

Isothermal decomposition data [a]

Substance No. (Table 1)	Additional substance [b] (weight, mg)	V_{Ar} (cm^3 min^{-1})	T (K)	m (mg)	ν (mole %)
1		200	415	80	84
			530		52
2		200	445	80	35
			510		35
3		200	485	80	100
			665		24
4		200	400	80	67
			530		39
5		200	445	80	16
			515		8
6		200	500	80	5
			585		3
7		200	415	80	57
			555		51
8		200	445	80	64
			515		43
9		200	495	80	50
			565		25
10		200	435	80	95
			525		51
11		200	425	80	85
			515		52
12		200	405	80	93
			575		67
13		200	425	80	83
			525		51
14		200	475	80	8
			545		4
15					
16		200	415	80	94
			555		77
17		200	455	80	100
			555		53
18		200	405	80	85
			575		52

TABLE 3 (Continued)

Substance No. (Table 1)	Additional substance [b] (weight, mg)	V_{Ar} (cm^3 min^{-1})	T (K)	m (mg)	ν (mole %)
19		200	400	80	81
			545		58
20		20	385	80	73
		200			83
	$PbCl_2$ (400)				75
	(c-$C_6H_{11}NH_3$)Cl (160)				79
		20	535	80	38
		200			78
	$PbCl_2$ (400)				67
	(c-$C_6H_{11}NH_3$)Cl (160)				45
21		200	395	80	88
			455		80
			570		71
22		20	415	80	25
		200			51
				320	48
				640	38
	$PbCl_2$ (400)			80	44
	($C_5H_{10}NH_2$)Cl (160)				33
		20	545		31
		200			55
				320	46
				640	42
	$PbCl_2$ (400)			80	32
	($C_5H_{10}NH_2$)Cl (160)				44
23		200	455	80	24
			515		19
			600		16

[a] V_{Ar} is the argon flow rate through the reactor. T is the temperature of thermolysis. For a given substance the thermolysis temperatures were chosen on the basis of the TG curve. In most cases they refer roughly to $T_{\alpha=0.2}$ and $T_{\alpha=0.8}$, if α corresponds to the total weight loss upon heating of a given compound to 700 K. m is the sample weight. ν is the mole % of liberated oxidant, 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.

gaseous phase are considered and may change with the extent of substitution of N–H by alkyl groups. These changes can be expected, however, to be rather small and this implies that chlorination of amines should proceed easily in our experimental conditions. On the other hand, thermochemical data suggest that thermal stability of chloramines decreases with the extent of substitution [23]. Thus, these derivatives should instantaneously undergo further transformations leading to more stable products, e.g. according to reaction (2)

$$2NCl_{3(l)} \rightarrow N_{2(g)} + 3Cl_{2(g)} \qquad \Delta H = -460 \text{ kJ mol}^{-1} \tag{2}$$

Protonated amines are, generally, more resistant toward reaction with chlorine than are non-protonated forms. Thus the chlorination processes occurring with the participation of the condensed phase are unlikely. Nonetheless, such processes cannot be excluded and they may, at least in part, be responsible for the differences in the behaviour of individual hexachloroplumbates during thermolysis. If chloramines are considered only as intermediate forms one can expect chlorination processes to be highly exothermic. Indeed, exothermic effects have been observed in DTA curves of some of the compounds studied (Table 1). This effect was particularly pronounced when a relatively large sample of the hexachloroplumbate of 1-azabicyclo[2.2.2]octane was analysed in a platinum crucible (Table 1).

Taking into account these considerations the primary processes during decomposition of alkanaminium hexcahloroplumbates can be expressed by reactions (2) and (3)

(i) first step

$$(R_pNH_{4-p})_2PbCl_{6(c)} \rightarrow Cl_{2(g)} + \left[PbCl_2 + 2(R_pNH_{4-p})Cl\right]_{(s)} \tag{3}$$

(ii) second step

$$\left[PbCl_2 + 2(R_pNH_{4-p})Cl\right]_{(s)} \rightarrow PbCl_{2(c)} + 2R_{p-a}NH_{3-p+a(g)} + 2(1-a)HCl_{(g)} + 2aRCl_{(g)} \tag{4}$$

where $a = 0$ for primary, secondary, and tertiary alkanaminium hexachloroplumbates and $a = 1$ for quaternary salts. For individual compounds two reaction stages may overlap. Moreover, the overall process can be complicated by the participation of chlorination processes. In consequence, many of the compounds studied show unique behaviour upon heating and only qualitative comparison of their thermal properties is possible. In fact all primary derivatives present a fairly simple decomposition pattern [6]. The course of thermolysis becomes more complex with an increase in the degree of substitution and with an increasingly complex alkyl group. An example of a compound exhibiting a complex thermal decomposition pattern is given in Fig. 2B.

Specific temperatures of thermolysis give a picture characteristic of a given compound, but some general features can be seen. Temperatures at which the onset of decomposition ($T_{0.01}$) occurs increase gradually in the order: primary < secondary < tertiary < quaternary hexachloroplumates. The peak temperatures in DTG and DTA also roughly follow this order. For quaternary salts, however, $T_{0.01}$ values are always markedly higher than those of other compounds in the series. The same trend has also been observed upon thermal decomposition of appropriate chloride salts [11].

Decomposition of some of the compounds studied is preceded by melting and presumably even phase transition. These features of hexachloroplumbates have not been examined in detail.

Some aspects of thermal decomposition of methyl-substituted aminium hexachloroplumbates have been examined previously [24]. Although those investigations were conducted in different experimental conditions they lead essentially to the same conclusions.

2. *Thermochemistry of alkanaminium hexachloroplumbates*

Various relations between thermochemical quantities for the compounds studied can be conveniently presented in the form of a thermochemical cycle (Fig. 3). All magnitudes shown in the cycle refer to 298 K and 1 atm: ΔH_f denotes the enthalpy of formation of a given substance; $U + 3RT$ is the lattice enthalpy; U represents the lattice energy; ΔH_d denotes the enthalpy of the thermal decomposition of hexachloroplumbate; and ΔH_v is the enthalpy of volatilization of alkanaminium chloride.

From the thermochemical cycle the following two relationships result

$$\begin{aligned}\Delta H^0_{f,c}\left[(R_pNH_{4-p})_2PbCl_6\right] &= 2\Delta H^0_{f,g}\left[R_pNH^+_{4-p}\right] + \Delta H^0_{f,g}\left[PbCl_6^{2-}\right]\\ &\quad - U^0\left[(R_pNH_{4-p})_2PbCl_6\right] - 3RT \qquad (5)\end{aligned}$$

$$\begin{aligned}\Delta H^0_d\left[(R_pNH_{4-p})_2PbCl_6\right] &= \Delta H^0_{f,g}[Cl_2] + \Delta H^0_{f,c}[PbCl_2]\\ &\quad + 2\Delta H^0_{f,g}\left[R_{p-a}NH_{3-p+a}\right] + 2(1-a)\Delta H^0_{f,g}[HCl] + 2a\Delta H^0_{f,g}[RCl]\\ &\quad - 2\Delta H^0_v\left[(R_pNH_{4-p})Cl\right] - \Delta H^0_{f,c}\left[(R_pNH_{4-p})_2PbCl_6\right] \qquad (6)\end{aligned}$$

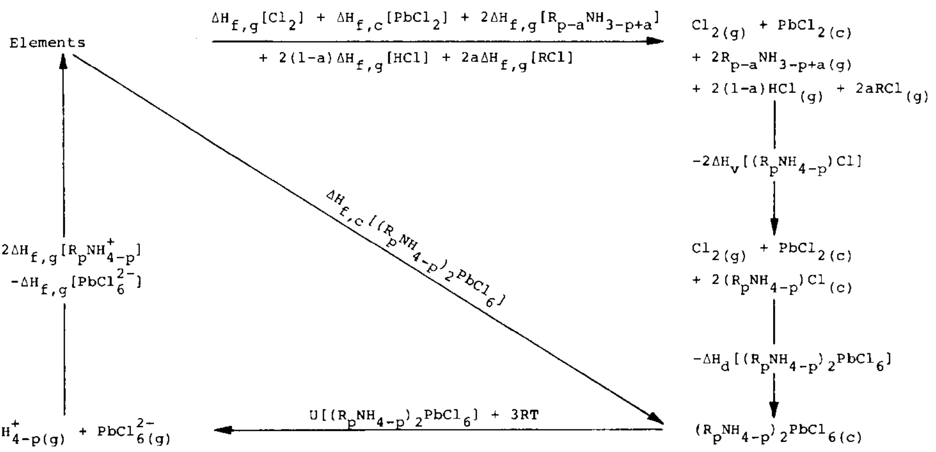

Fig. 3. The thermochemical cycle ($a = 0$ in the case of primary, secondary, and tertiary hexachloroplumbates and $a = 1$ for quaternary salts).

In order to evaluate numerical values of both quantities defined by eqns. (5) and (6) it is necessary to know the values for the crystal lattice energy of alkanaminium hexachloroplumbates. Unfortunately, only the value of U for $(NH_4)_2PbCl_6$ has so far been reported [25]. To determine values we invoked the approximate method developed originally by Kapustinskii [26] and improved later by Yatsimirskii [27]. According to these authors the crystal lattice energy can be expressed with the equation [27]

$$U = 120.2\frac{(\Sigma n)Z_K Z_A}{r_K + r_A}\left[1 - \frac{0.0345}{r_K + r_A} + 0.087(r_K + r_A)\right] \quad \text{in kJ mol}^{-1} \tag{7}$$

where (Σn) is the total number of ions in the simplest formula unit of the molecule; Z_K and Z_A denote the numerical values of the charges of cation and anion, respectively; and r_K and r_A are the "thermochemical" ionic radii (in nm). For $r_{PbCl_6^{2-}}$ we assumed a value equal to 0.372 nm which was derived from eqn. (7) taking values of crystal lattice energies for rubidium, caesium, and ammonium hexachloroplumbates from ref. 25 and appropriate ionic radii of Rb^+, Cs^+, and NH_4^+ from ref. 5. Combining these values with values of r_K listed in Table 4 we estimated crystal lattice energies for all hexachloroplumbates examined in this and our previous work [6]. They are listed in Table 4.

The enthalpy of formation of crystalline hexachloroplumbates can be now evaluated from eqn. (5) assuming for $\Delta H^0_{f,g}[PbCl_6^{2-}]$ a value equal to -940 kJ mol^{-1} [25]. Further thermochemical information regarding this group of compounds can be obtained by calculating the enthalpy of the thermal dissociation of the salts from eqn. (6). For this purpose we used necessary ancillary data from Table 4 and the following values of heats of formation of reactants (in kJ mol^{-1}): -359, -92, -82, -112, -132, and -155 for $PbCl_{2(c)}$ [23], $HCl_{(g)}$ [23], $CH_3Cl_{(g)}$ [29], $C_2H_5Cl_{(g)}$ [29], n-$C_3H_7Cl_{(g)}$ [29], and n-$C_4H_9Cl_{(g)}$ [29], respectively. The derived values of both quantities are shown in Table 4.

Crystal lattice energies of alkanaminium hexachloroplumbates generally decrease with an increase in the size of the alkyl substituent and with an increase in the number of alkyl groups attached to the nitrogen atom. Both these trends agree with eqn. (7). However, values of U do not vary significantly and this is because differences between "thermochemical" radii of cations are relatively small, which implies that this quantity refers rather to the distances between charged centres in the crystal lattice than to the true dimensions of ions [3,11,28].

The enthalpy of formation of crystalline alkanaminium hexachloroplumbates is characteristic of a given compound, but some regularities may be seen. Plotting $\Delta H^0_{f,c}[(R_pNH_{4-p})_2PbCl_6]$ against the number of alkyl substituents (p), in the series of unbranched alkanaminium salts, gives a nearly linear decrease of values of this quantity in the range of p between 1 and 4. Values of $\Delta H^0_{f,c}$ decrease gradually with increasing size of the alkyl group in

TABLE 4

Thermal characteristics for alkanaminium hexachloroplumbates

Substance			$R_{p-a}NH_{3-p+a}$	$R_pNH_{4-p}^+$		$(R_pNH_{4-p})Cl$	$(R_pNH_{4-p})_2PbCl_6$			
R[b]	p	a	$\Delta H^0_{f,g}$ [11,27,28] (kJ mol^{-1})	r [3,11] (nm)	$\Delta H^0_{f,g}$ [11,29] [c] (kJ mol^{-1})	ΔH^0_v [11,29] (kJ mol^{-1})	U^0 (kJ mol^{-1})	$\Delta H^0_{f,c}$ (kJ mol^{-1})	ΔH^0_d (kJ mol^{-1})	
									A[d]	B[e]
H	0	0	−46	0.145	630	168	1365	−1052	81	
CH_3	1	0	−23	0.179	605	157	1290	−1027	124	
CH_3	2	0	−19	0.188	584	167	1271	−1050	135	
CH_3	3	0	−24	0.208	563	155	1232	−1053	152	
CH_3	4	1	−24	0.223	542	166	1205	−1068	165	
C_2H_5	1	0	−48	0.180	568	168	1288	−1099	124	
C_2H_5	2	0	−73	0.197	511	174	1253	−1178	141	
C_2H_5	3	0	−93	0.207	465	185	1234	−1251	152	
C_2H_5	4	1	−93	0.224	415	196	1203	−1320	159	
n-C_3H_7	1	0	−70	0.181	540	172	1286	−1153	126	68[g]
n-C_3H_7	2	0	−116	0.202	459	176	1244	−1273	146	107[f]
n-C_3H_7	3	0	−161	0.223	387	174	1205	−1378	165	
n-C_3H_7	4	1	−161	0.248	311	182	1161	−1486	177	
i-C_3H_7	1	0	−84	0.177	523	180	1294	−1195	124	78[f]
i-C_3H_7	2	0	−144	0.197	423	190	1253	−1354	143	

n-C_4H_9	1	0	−92	0.179	516	177	1290	−1205	124	110 [g]
n-C_4H_9	2	0	−157	0.195	414	190	1257	−1376	139	
n-C_4H_9	3	0	−222	0.257	321	139	1146	−1451	186	
n-C_4H_9	4	1	−222	0.271	225	158	1124	−1621	192	
i-C_4H_9	1	0	−100	0.179	507	178	1290	−1223	124	61 [f]
s-C_4H_9	1	0	−105	0.181	497	179	1286	−1239	128	
t-C_4H_9	1	0	−121	0.190	477	169	1267	−1260	137	
i-C_4H_9	2	0	−179	0.203	389	180	1242	−1411	150	
n-C_5H_{11}	1	0	−110	0.179	496	179	1290	−1245	124	125 [g]
i-C_5H_{11}	1	0	−121	0.179	483	180	1290	−1271	126	106 [f]
n-C_6H_{13}	1	0	−130	0.176	475	184	1296	−1293	122	111 [g]
n-C_7H_{15}	1	0	−151	0.179	454	181	1290	−1329	122	97 [g]
n-C_8H_{17}	1	0	−172	0.175	432	187	1298	−1381	120	83 [g]
c-C_6H_{11}	1	0	−105	0.181	494	183	1286	−1245	126	70 [f]
$\frac{1}{2}(C_4H_8)$ *	2	0	−3	0.192	583	178	1263	−1044	139	
$\frac{1}{2}(C_5H_{10})$ **	2	0	−49	0.187	533	190	1273	−1154	133	74 [f]
$\frac{1}{3}(C_7H_{13})$ ***	3	0	−4	0.197	553	200	1253	−1094	143	

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[b] Symbols denoted with asterisks represent pyrrolidine (*), piperidine (**), and 1-azabicyclo[2.2.2]octane (***) and their derivatives, respectively.

[c] The $\Delta H^0_{f,g}[R_pNH^+_{4-p}]$ values taken from ref. 28 were modified using more reliable data for the enthalpy of formation of appropriate amines [29,30].

[d] Values calculated from eqn. (6).

[e] Experimental values (estimated on the basis of eqn. (8)).

[f] From this work.

[g] From ref. 6.

the series of primary, secondary, tertiary, and quaternary alkanaminium hexachloroplumbates, although this dependency is not linear. An exception is ammonium hexachloroplumbate whose $\Delta H^0_{f,c}$ and U values do not correlate with those for other compounds. The enthalpy of formation of compounds possessing the same chemical formula decreases if the structure of alkyl substituents becomes more complex, e.g. $\Delta H^0_{f,c}$ values in the series of butanaminium hexachloroplumbates follow the order: *n*-Bu > *i*-Bu > *s*-Bu > *t*-Bu. The latter regularity is also valid for appropriate amines (see Table 4) and it agrees with the well-known empirical rule relating thermodynamic stability to the structure of isomeric derivatives.

Another quantity which was evaluated from the thermochemical cycle is the enthalpy of the thermal decomposition of hexachloroplumbates. Values for this quantity can be directly compared with those derived using the experimental α vs. T dependencies, i.e. from eqn. (8)

$$\ln \alpha = -\frac{\Delta H^0_d}{R}\frac{1}{T} + \text{const} \tag{8}$$

Reviewing data listed in the last two columns of Table 4 it may be seen that the agreement between these two sets of ΔH^0_d values is rather poor. Only 1-pentanaminium hexachloroplumbate values obtained by the application of both procedures show satisfactory agreement. There are several reasons for the observed discrepancies. Estimations based on the thermochemical cycle require that all reactants remain in their standard states and that they do not interact with each other. The compounds studied decompose at relatively low temperatures. Furthermore, all experiments were conducted under atmospheric pressure. Therefore ΔH^0_d values derived from eqn. (8) correspond roughly to the standard conditions. However, the expected solid products, i.e. $PbCl_2$ and amine hydrochlorides, can interact with each other in condensed phases. If the mixed salts are formed instantaneously with the decomposition of parent molecules the enthalpy gaps corresponding to reaction (3) would be lower than ΔH^0_d values from the thermochemical cycle since the system would not attain the enthalpy level of the pure components. The enthalpy changes corresponding to the above effect are difficult to assess and, thus, it is impossible to estimate how they affect those evaluated using ΔH^0_d values derived from eqn. (8). Data in Table 4 seem to indicate that the formation of double salts is a major factor influencing experimental values for the enthalpy of the thermal decomposition. There is a further restriction on the applicability of eqn. (8). This equation can be used only if the system attains equilibrium at a given temperature. It is difficult to predict how far this is accomplished in our experiments. However, if the process occurs very far from equilibrium it would involve the existence of an activation barrier higher than ΔH^0_d. In such conditions the application of eqn. (8) would lead to higher ΔH^0_d values, which does not agree with the results of our investigations. This discussion implies that values of ΔH_d^0 derived from eqn. (8) can be considered as rough estimates. Therefore, only qualitative agreement between both sets of ΔH_d^0 values can be expected and this is demonstrated by the data listed in Table 4.

Values for the enthalpy of the thermal dissociation of alkanaminium hexachloroplumbates, directly (from eqn. (8)) and from the thermochemical cycle (eqn. (6)), are positive. This means that all the compounds studied are thermodynamically stable. Indeed, these derivatives easily crystallize from aqueous solution containing both cations and $PbCl_6^{2-}$ anion in appropriate concentrations by acidifying with HCl. On the other hand, many hexachloroplumbates, particularly those possessing long alkyl substituents, slowly decompose in the solid state, gradually losing Pb(IV). At least two effects contribute to this. Firstly, decomposition according to eqn. (3) is likely since the enthalpy change corresponding to this process is relatively low, and the system can gain enough energy from the environment to overcome the thermochemical barrier for the decomposition, even at ambient temperature. Reaction (3) is irreversible in the solid phase since chlorine is removed instantaneously from the reaction zone. Thus, a molecule cannot return to the primary state once it has undergone destruction. Another possibility for acceleration of decomposition of hexachloroplumbates is the fact that chlorination processes can occur in condensed phases. These processes have not been included in thermochemical cycle. However, from our previous considerations they could cause the thermochemical barrier for the decomposition to become lower than that predicted for reaction (3) or even cause it to become negative as the majority of chlorination processes are exothermic. Such processes could proceed also inside the crystal lattice without release of chlorine. We believe the latter effect is mostly responsible for differences in the behaviour of individual alkanaminium hexachloroplumbates upon storage.

3. *Kinetics of the thermal decomposition*

To obtain further information on the thermal behaviour of the compounds studied we attempted to examine the kinetics of the first step of the decomposition of some hexachloroplumbates which show well-defined reaction stages (Table 2). For this purpose four methods were applied to evaluate kinetic constants together with 14 integral functions corresponding to certain kinetic models for the process. These methods have been discussed in detail elsewhere [6]. To facilitate discussion we present in Table 5 a full set of the results of these calculations for 3-methyl-1-butanaminium hexachloroplumbate. Furthermore, selected kinetic data for the remaning five compounds listed in Table 2 are compiled in Table 6.

In searching for an adequate model for the thermal process, i.e. the form of the $g(1-\alpha)$ function, we examined the statistical functions $|r|$ and δ. These functions attain values equal to 1 and 0, respectively, if a given model

TABLE 5

Kinetic parameters for the thermal decomposition of 3-methyl-1-butanaminium hexachloroplumbate [a]

Kinetic model [b]	Method of calculation [6]											
	A: $\ln g(1-\alpha)/T^2$ $= \ln ZR/(\phi E) - E/(RT)$			B: $\ln g(1-\alpha)/T$ $= \ln Z/\phi - E/(RT)$			D [c]: $Z = \phi R/E$ $\times g(1-\alpha)/p(x)$			E: $Z = \phi/T$ $\times g(1-\alpha)/\exp(-E/(RT))$		
	E	Z	$\|r\|$	E	Z	$\|r\|$	E	Z	δ	E	Z	δ
R1	99.6	6.4 10	0.99392	103	5.6 09	0.99432	100	7.7 10	0.067876	103	5.9 09	0.067709
R2	118	1.2 13	0.99929	121	8.8 11	0.99933	118	1.4 13	0.027836	121	9.4 11	0.027685
R3	124	7.5 13	0.99980	128	5.2 12	0.99981	125	9.4 13	0.015990	128	5.9 12	0.015902
P1	73.1	1.6 07	0.99362	76.3	1.9 06	0.99419	73.5	1.9 07	0.051429	76.5	2.0 06	0.051264
P2	64.3	9.6 05	0.99347	67.5	1.3 05	0.99412	64.7	1.2 06	0.045882	67.6	1.4 05	0.045719
P3	46.6	3.4 03	0.99298	49.8	6.3 02	0.99392	47.0	4.4 03	0.034688	49.9	6.5 02	0.034532
P4	20.1	4.9−01	0.99038	23.3	2.1−01	0.99298	20.7	7.8−01	0.017644	23.3	2.1−01	0.017510
F1	139	3.0 16	0.99880	143	1.9 15	0.99884	139	2.8 16	0.043852	143	2.1 15	0.044020
A2	66.5	2.8 06	0.99871	69.7	3.7 05	0.99880	66.7	3.3 06	0.021629	69.7	3.7 05	0.021800
A3	42.2	1.0 03	0.99860	45.4	2.1 02	0.99876	42.6	1.4 03	0.014296	45.4	2.1 02	0.014453
D1	206	1.0 25	0.99432	209	4.3 23	0.99451	207	1.7 25	0.130766	210	6.3 23	0.130600
D2	228	6.3 27	0.99795	231	2.4 26	0.99801	228	7.6 27	0.088289	232	3.6 26	0.088109
D3	255	1.1 31	0.99981	258	3.8 29	0.99982	255	1.1 31	0.031578	259	4.5 29	0.031528
D4	237	2.7 28	0.99894	240	9.9 26	0.99898	237	3.1 28	0.066739	240	1.1 27	0.066608

[a] E = apparent activation energy (kJ mol^{-1}); Z = constant (s^{-1}); $|r|$ = linear correlation coefficient; $\delta = [1/N\Sigma_{i=1}^{N}(Z_i - Z)^2]^{1/2}$ and $Z = 1/N\Sigma_{i=1}^{N}Z_i$ (where N = number of experimental data points). $\phi = 4.5$ K min^{-1}. Values of Z are presented in computer notation, e.g. $-1.00-05 = -1.00\times10^{-5}$.

[b] Ref. 10, Table 1.

[c] Values of $p(x)$ function were calculated on the basis of 10 truncated parts of a Legendre fraction expansion series [31].

TABLE 6

Kinetic constants for the thermal dissociation of some alkanaminium hexachloroplumbates [a]

Substance No. (Table 1)	ϕ (K min^{-1})	Kinetic model [a]	Method of calculation [a]			
			D		E	
			E	*Z*	*E*	*Z*
7	4.4	R1	100	4.1 10	103	3.1 09
		R2	117	5.0 12	120	3.3 11
		R3	124	3.2 13	127	2.0 12
		F1	138	8.7 15	141	4.9 14
		D3	254	1.7 30	257	5.4 28
10	4.4	R1	70.6	9.9 05	73.8	1.1 05
		R2	84.1	3.3 07	87.3	3.2 06
		R3	89.2	1.1 08	92.5	1.0 07
		F1	101	1.2 10	104	9.4 08
		D3	185	3.2 19	188	1.4 18
15	5.0	R1	55.4	8.5 04	58.2	1.1 04
		R2	65.5	1.5 06	68.4	1.6 05
		R3	69.4	3.9 06	72.2	3.9 05
		F1	77.9	2.2 08	80.8	2.1 07
		D3	145	4.1 16	148	2.2 15
20	4.7	R1	64.2	5.6 05	67.2	6.5 04
		R2	75.5	1.2 07	78.5	1.2 06
		R3	79.8	3.4 07	82.8	3.3 06
		F1	89.4	2.5 09	92.4	2.1 08
		D3	166	3.2 18	169	1.5 17
22	5.2	R1	68.0	8.4 05	71.0	9.3 04
		R2	79.9	1.9 07	83.0	1.9 06
		R3	84.5	5.5 07	87.7	5.3 06
		F1	94.8	4.4 09	98.0	3.8 08
		D3	176	8.5 18	179	3.8 17

[a] For explanation see Table 5.

fits perfectly the experimental data. However, the use of this criterion only may lead to misleading conclusions. Since for the description of the kinetic phenomena Arrhenius type equations were applied, the derived apparent activation energy refers to the energy barrier for the process. This approach also requires that there exists only one step which determines the kinetics of the process. From this it must be concluded that only such models for which corresponding *E* values are higher or eventually somewhat lower than the thermochemical barrier for the process have real physical meaning. If the activation barrier is much lower than ΔH the overall process would involve several steps to attain the energy level of the products. In these conditions the application of the Arrhenius model would not be justified. Moreover, more complex analysis would be necessary to describe the kinetics of such processes. For these reasons P1, P2, P3, P4, A2, and P3 reaction models have been excluded from further consideration.

The results of calculations for all six compounds examined seem to indicate that phase-boundary processes determine the kinetics of the thermal decomposition of hexachloroplumbates. There are some facts which support this concept. Firstly, $g(1-\alpha)$ functions corresponding to these models fit the experimental curves quite well. Secondly, these mechanisms predict the existence of a relatively small activation barrier over that resulting from the thermochemical requirements. Moreover, experimental conditions favour processes occurring on the surface of a condensed phase. For these reasons values of E and Z corresponding to R1, R2, and R3 mechanisms are listed in Table 6. Table 6 also includes kinetic constants for F1 and D3 reaction models to enable comparison of the data from this work with those for other hexachloroplumbates [6]. The diffusion models fit the experimental data poorly and it does not seem to be likely that the process can be realized for these pathways.

Data in Table 6 demonstrate that values of E generally follow the same trends as ΔH_d^0 values. On the other hand Z is a rather mathematical constant without true physical significance, and as shown in Tables 5 and 6 values of this quantity depend markedly on the mathematical method applied.

Taking into account these considerations it may be concluded that an R2 mechanism most probably controls the kinetics of the thermal decomposition of the compounds studied. This means that a molecule has to overcome only a slightly higher activation barrier than that resulting from ΔH_d^0. This tends to confirm the conclusions of the previous section regarding the thermal stability of hexachloroplumbates.

4. Further remarks

Four methods chosen in this work to examine the kinetics of the thermal processes are based on the integral type equations, although they do not have the same origin. Methods A and D are based on the assumption that the rate of non-isothermal processes can be expressed with eqn. (9)

$$\frac{d\alpha}{dT} = \frac{Z}{\phi} f(1-\alpha)\exp(-E/RT) \tag{9}$$

which results from the isothermal rate equation by substituting $dt = dT/\phi$ (method A is known as Coats and Redfern's method [33]). On the other hand, methods B and E proceed from the assumption that the extent of reaction is a function of both time and temperature and thus the rate equation can be written in the form [32]

$$\frac{d\alpha}{dT} = \frac{1}{\phi}\left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial T}\right)_t \tag{10}$$

Despite obvious differences in the origin of both approaches and differences in the computational procedures applied, the apparent activation energies derived do not differ significantly. Differences in the Z constant are more pronounced. Methods based on eqn. (10) always yield lower Z values. Interesting features show statistical functions $|r|$ and δ. Correlation coefficients are always somewhat higher in the case of method B than A. On the other hand, values of the δ function do not permit one to judge whether method D or E is a better approximation of the experimental data. Method D can be considered accurate from a computational point of view since values of $p(x)$ were calculated from the Legendre series [31], which approximates the latter function precisely.

It is apparent from this study and our previous study [6] that both methods describe the experimental data equally well. Also the derived kinetic constants are very similar. This implies that both eqn. (9) and eqn. (10) can be applied to the description of kinetic phenomena under non-isothermal conditions.

We intend to comment on the latter point particularly in view of recent criticism of eqn. (10) by some authors [34,35]. To prove that eqn. (10) is unsound Kemeny and Granasy have shown recently [34] (Fig. 2) that eqn. (11)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{Z}{\phi} f(1-\alpha)\left(1 + \left((T-T_0)/T^2\right)E/R\right) \exp(-E/RT) \qquad (11)$$

which results directly from eqn. (10) [32], would lead to a much higher rate of reaction than that predicted from isothermal measurements. Unfortunately, this cannot be considered as proof of the non-validity of eqn. (10) since the authors compared in their work two different physical quantities, namely $\mathrm{d}\alpha/\mathrm{d}t$, which according to the classical definition expresses the rate of the process, and $\mathrm{d}\alpha/\mathrm{d}T$ (actually in eqn. (6*) [34] the authors show $\phi \mathrm{d}\alpha/\mathrm{d}T = \mathrm{d}X/\mathrm{d}t$), which can be called a rate for non-isothermal processes. The assumption which the authors made, i.e. $\mathrm{d}T = \phi \mathrm{d}t$, is inappropriate (in the case of eqn. (6*) [34]) since treating α as a function of t and T, values of the non-isothermal extent of the reaction refer to different temperatures, and not time, and therefore the proper form of the kinetic equation is that shown by (10) and consequently (11). We would like to point out that time is not a parameter which describes the behaviour of the system in non-isothermal experiments. What we really measure in these conditions is $\mathrm{d}\alpha/\mathrm{d}T = f(T)$ and $\alpha = f(T)$. Thus, optional transformations of $\mathrm{d}\alpha/\mathrm{d}T$ to $\mathrm{d}\alpha/\mathrm{d}t$ by substituting $\mathrm{d}T/\mathrm{d}t = \phi$, particularly in the case of eqn. (10), are unjustifiable. If $\alpha = f(t, T)$ the rate of reaction, in the classical meaning, is given by the partial derivative $(\partial\alpha/\partial t)_T$ which is actually expressed by the same equation as the rate of isothermal processes. Therefore, using eqn. (10), identical values of the rate of the process for isothermal and non-isothermal conditions would be obtained.

Instead of the procedure presented in ref. 34 it would be more appropriate to compare kinetic constants derived by methods based on both eqn. (9) and eqn. (10) with those resulting from isothermal measurements. The kinetic constants, corresponding to certain reaction models, are actually only important characteristics for the compounds or systems studied and so far this information only has been collected in the literature.

We have shown earlier [32] that the reference point in non-isothermal conditions is best assumed to be 0 K. Such an assumption was made several years ago for the temperature integral, i.e. $\int_{T_0}^{T} \exp(-E/RT)$, and we do not see any reason why the integral $\int_{T_0}^{T} \mathrm{d}T$, which occurs during the derivation of eqn. (11) [32], should be treated differently. Furthermore, the reference point for temperature must be the same for any system investigated and cannot depend on individual features of a given substance (e.g. T_0 cannot correspond to the onset of decomposition, equilibrium temperature, etc.). This implies that experiments whose primary objectives are kinetic investigations should be conducted in such a way as to enable the temperature growth of the system starting from absolute zero. Thus, measurements carried out in hyperbolic heating programmes are not adequate for kinetic study [32]. From this point of view the considerations in the Appendix of ref. 34 do not provide proof of the non-validity of eqn. (10).

The workers questioning the validity of eqn. (10) voice one main objection, viz. α is not a state function. It is obvious that this quantity depends on the reaction pathway and thus, it is not a state function in a thermodynamical sense. We do not agree, however, that it is unjustifiable to express α as a total differential with t and T. Widely used descriptions of kinetic phenomena are based on the Arrhenius model. The basic assumption of this approach is that there exists a "bottleneck" for the process, i.e. only one pathway which controls the rate of the process. The mathematical description of the reaction pathway is given by the form $g(1-\alpha)$ or $f(1-\alpha)$. Furthermore, values of E and Z correspond only to a given reaction model. Taking into account these considerations eqn. (10) is valid and this results from the application of strict mathematical rules to the expression for isothermal conditions [32]. We would like also to emphasize that without such an assumption there would be no reason to collect kinetic information.

The discussion of basic problems of chemical kinetics was not a primary objective of this work. We have analysed briefly some of these which link directly to our study. We intend to present more details regarding this subject in a separate note.

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