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THERMAL REACTIONS OF LEAD(IV) CHLORIDE COMPLEXES IN THE SOLID STATE. PART III. THERMOLYSIS OF AMMONIUM AND METHYL-SUBSTITUTED AMMONIUM HEXACHLOROPLUMBATES

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ABSTRACT

Ammonium and methylammonium hexachloroplumbates of general formula $[(CN_3)_nNH_{4-n}]_2PbCl_6$, with $n = 0$—4, undergo thermal decomposition on heating to 720 K. The thermal processes are studied by differential thermal analysis and thermogravimetry. Isothermal experiments are done in an apparatus which permits a quantitative determination of some of the products. Thermolysis occurs in two steps: (i) liberation of chlorine $[(CH_3)_nNH_{4-n}]_2PbCl_6(s,l) \rightarrow PbCl_2(s) + 2\ [(CH_3)_nNH_{4-n}]Cl(s) + Cl_2(g)$; (ii) thermal processes which occur on heating the solid products of the above reaction; for compounds with $n = 0$—3, the process is described by, $PbCl_2(s) + 2\ [(CH_3)_nNH_{4-n}]\ Cl(s) \rightarrow PbCl_2(s) + 2(CH_3)_nNH_{3-n}(g) + 2\ HCl(g)$. When the second reaction is slow in the temperature range of the first, chlorine is rapidly evolved and stoichiometric amounts discharged at stage (i). If this condition is not satisfied, secondary reactions occur, mostly in the gas phase, which consume chlorine.

INTRODUCTION

Among the solid derivatives of hexachloroplumbic acid, the hexachloroplumbates of aliphatic amines have been most extensively studied [1]. These have been used in the preparation of lead(IV) chloride [1,2] and other derivatives of hexachloroplumbic acid [1], for use as model compounds in studying the structure of hexachloroplumbates [3,4], in the determination of some thermodynamic parameters of $PbCl_4$ and $PbCl_6^{2-}$ [1], and for other purposes. These compounds are known to undergo slow decomposition at room temperature, gradually losing their oxidative power [1]. However, data on the thermal decomposition are only fragmentary.

In a continuation of studies on the thermal behaviour of solid complexes of $PbCl_4$ and H_2PbCl_6 [5,6], we have investigated the thermolysis of the hexachloroplumbates of ammonia and simple aliphatic amines.

EXPERIMENTAL

Hexachloroplumbic acid and its ammonium and methylammonium salts were prepared by the methods already described [1,5]. Thermal analyses were done on a Monikon OD-103 derivatograph. Other measurements and analyses were done by methods already described [5,6].

RESULTS AND DISCUSSION

The results of the thermal analyses of ammonium and methylammonium hexachloroplumbates are shown in Table 1 and Fig. 1. Thermal decomposition is not preceded by melting; on DTA curves there are endothermic peaks only. With respect to temperature at the beginning of the decomposition, $T_{\alpha=0.01}$, and those corresponding to the first endothermic DTA (and DTG) peaks, the compounds can be ranked in the following order: $(NH_4)_2PbCl_6$ > $[(CH_3)_4N]_2PbCl_6$ > $[(CH_3)_3NH]_2PbCl_6$ > $[(CH_3)_2NH_2]_2PbCl_6$ > $(CH_3NH_3)_2$-$PbCl_6$. If these two temperatures are considered as criteria of the thermal stability of the compounds, the position of ammonium hexachloroplumbate in this series appears to be abnormal.

The basicity of aliphatic amines is known to increase with increasing number of methyl groups attached to the nitrogen atom [7]. The basicity constants of NH_4OH, $(CH_3NH_3)OH$, $[(CH_3)_2NH_2]OH$ and $[(CH_3)_3NH]OH$ at 298 K are [8]: 1.8×10^{-5}, 4.38×10^{-4}, 5.1×10^{-4} and 5.3×10^{-5}, respectively. The tetramethylammonium base has been placed among the strong electrolytes, its basicity constant being greater than those of the other methylammonium bases by almost four orders of magnitude [7]. The stability of the ammonium and methylammonium hexachloroplumbates should depend, among other factors, on the relative energy of interaction of the appropriate ions [9]. Accordingly, ammonium hexachloroplumbate should be the least stable. A similar effect on the stability of these compounds should be exerted by cation size [1]. As these features fail to explain the extraordinary stability of the ammonium salt, it seems likely that there are other reasons which explain the remarkable differences in the properties of

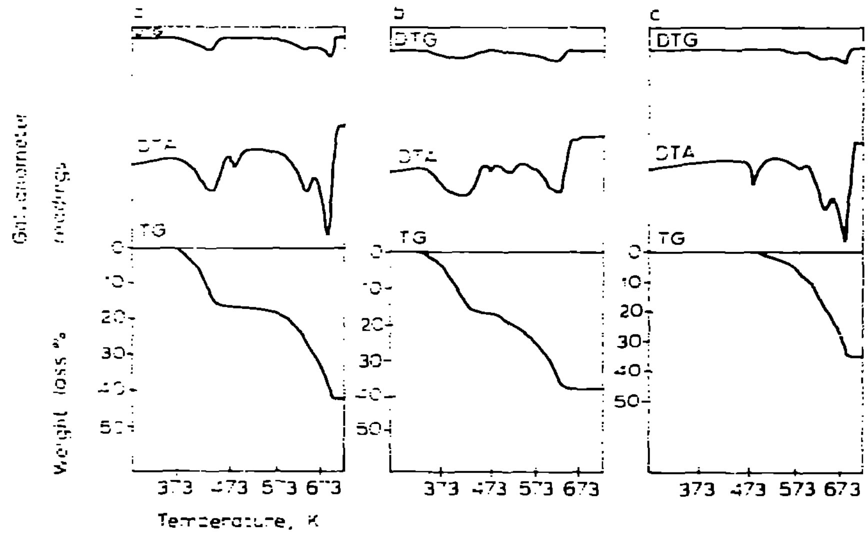

Fig. 1. Thermal analysis of $[(CH_3)NH_3]_2PbCl_6$ (cf. Table 1).

NH_3 and methylamines. Similar anomalies have been observed in melting points and temperatures of phase transitions of ammonium chloride and methylammonium chlorides [10].

It is worth noting that the results of thermal analyses are identical in nitrogen and in air. Moreover, results are qualitatively similar whether the sample is in the form of a thick layer in a ceramic crucible or placed on five platinum plates. In the latter case, lower transition temperatures are usually observed. These findings show the course of the thermal processes to be virtually independent of reaction conditions.

The results of the thermal analyses allow two steps in the thermal decomposition of hexachloroplumbates to be distinguished: (i) loss of chlorine

$$[(CH_3)_nNH_{4-n}]_2PbCl_6(s) \rightarrow PbCl_2(s) + 2[(CH_3)_nNH_{4-n}]Cl(s) + Cl_2(g) \qquad (1)$$

accompanied always by the first endothermic DTA (and DTG) peak, and (ii) processes which occur on heating the products of reaction (1).

Heating $PbCl_2$ from 298 K to 768 K does not bring about phase transformation [11]. In contrast, both ammonium and methylammonium salts undergo various phase transformations owing to changes in their crystal lattice [12]. These processes have been extensively studied for chlorides [10—18] and other ammonium salts [12,19]. The transition temperatures for the ammonium and methylammonium chlorides are shown in the final column of Table 1. As seen, effects due to structural changes of the chlorides formed in reaction (1) could not be observed in the DTA curves, because the respective temperatures were invariably lower than those corresponding to decomposition of the hexachloroplumbates. Nevertheless methylammonium, dimethylammonium and trimethylammonium chlorides were found to melt in their mixtures with $PbCl_2$.

In individual series of measurements the salts were heated in the oven of the derivatograph until the first step was complete. After cooling, the samples were re-analyzed, no transformations due to changes in the crystalline structure of the ammonium and methylammonium chlorides being noted. However, peaks due to melting of the chlorides appeared. This indicates that on cooling, the structure of high-temperature modifications is retained.

Further heating resulted in volatilization of the ammonium and methylammonium salts. For compounds with $n = 0$—3, the following general equation is suggested

$$PbCl_2(s) + 2[(CH_3)_n NH_{4-n}]Cl(s,l) \rightarrow PbCl_2(s) + 2(CH_3)_nNH_{3-n}(g) + 2HCl(g) \qquad (2)$$

These processes are accompanied by the corresponding DTA (and DTG) peaks. It is interesting that while sublimation of the ammonium and methylammonium chlorides in mixtures with $PbCl_2$ is a multistage process, sublimation of ammonium chloride occurs in one step [13]. The complex course of the sublimation is apparently due to the presence of $PbCl_2$. However, the thermal analysis data rule out the possibility of formation of any unidentified compound in the solid state in reaction (1).

Volatilization of ammonium and methylammonium chlorides is accompa-

TABLE 1

Thermal analysis data [a]

Substance	Sample weight (mg)	Sample holders [b]	Temperature (K) and character of endothermic peaks in DTA [c]	Peak temperature in DTG (K)
$(NH_4)_2PbCl_6$	1200	C	505m	495
			630s; 665m (unresolved)	625; 660
	1200	P	495m	485
			575s; 605s (unresolved)	570; 595
$2NH_4Cl + PbCl_2$	1013.2	C	470m (phase transition)	645; 675
			650s; 680m (unresolved)	
$(CH_3NH_3)_2PbCl_6$	800	C	430m	425
			480w	
			635m; 675s (unresolved)	620; 685
	450	C	425m	420
			475w	
			625w; 680s (unresolved)	620; 680
	800	P	415s	405
			475w	
			515w	515
			615s; 625s (unresolved)	610; 620
$2CH_3NH_2 \cdot HCl + PbCl_2$	682.6	C	480w (melting)	
			585w	580
			635m; 680s (unresolved)	625; 685
$[(CH_3)_2NH_2]_2PbCl_6$	400	C	435m	430
			490w	
			615m; 645w (unresolved)	625
	400	P	430m	425
			485w	
			565m	570
$2(CH_3)_2NH \cdot HCl + PbCl_2$	344.6	C	453w (melting)	
			615m; 660w (unresolved)	620; 655

Temperature [5]		Weight loss (%)						Fig.	Temperature (K) of the phase transition of $[(CH_3)_n\text{-}NH_{4-n}]Cl$ [10]
of the initial decomposition (K) $T_{\alpha=0.01}$	at which decomposition complete (K) $T_{\alpha=0.99}$	1st stage		2nd stage		total			
		from TG	theoretical [d]	from TG	theoretical [e]	from TG [f]	theoretical [g]		
435	670	21	15.5	18	23.5	39	39.0		
405	625	23	15.5	16	23.5	39	39.0		
475	695								243 (II—III transition) 457 (I—II transition 613 (sublimation)
370	700	16	14.6	26	27.9	42	42.5	1a	
355	685	15	14.6	28	27.9	43	42.5		
345		17	14.6	23	27.9	40	42.5	1b	
485	695							1c	223 (II—III transition) 263 (I—II transition) 499 (melting)
375		14	13.8	29	31.8	43	45.6		
365	620	17	13.8	29	31.8	46	45.6		
475	685								260 (II—III transition) 313 (I—II transition) 444 (melting)

TABLE 1 (continued)

Substance	Sample weight (mg)	Sample holders [b]	Temperature (K) and character of endothermic peaks in DTA [c]	Peak temperature in DTG (K)
$[(CH_3)_3NH]_2PbCl_6$	800	C	460m	460
			570m; 635s; 665w (unresolved)	625; 650
	800	P	450m	460
			520s; 570m; 580m (unresolved)	540; 565; 580
$2(CH_3)_3N \cdot HCl + PbCl_2$	694.8	C	555m (melting)	
			610w; 640m; 655w (unresolved)	580; 595; 610; 630: 655
$[(CH_3)_4N]_2PbCl_6$	500	C	530m: 560m: 585m; 615m (unresolved)	540: 560: 580; 615
			700s	695
	800	P	515m: 555m: 585m: 615m (unresolved)	535: 555: 580; 610
			695s	690
$2(CH_3)_4NCl + PbCl_2$	437.6	C	540m (phase transition)	
			625s	615
			695s	690

[a] The thermal analyses were made with a derivatograph in a dynamic atmosphere of nitrogen or air. α-Al_2O_3 served as reference. The sensitivities of the galvanometer were 1/5 and 1/20 for the DTA and DTG curves, respectively. All analyses were made at a heating rate of 5 K min^{-1}.

[b] C, ceramic crucible; P, five platinum plates.

nied by dissociation to the corresponding amines (ammonia) and HCl (eqn. (2)) [7]. However, for $[(CH_3)_nNH_{4-n}]Cl$, with n = 1—4, the following reaction is also possible

$$[(CH_3)_nNH_{4-n}]Cl \rightarrow (CH_3)_{n-1}NH_{4-n} + CH_3Cl \qquad (3)$$

When reaction (1) occurs at a much lower temperature than reaction (2), i.e. the two steps are not superimposed, both reactions can be recorded separately by thermal analysis, as has been shown in thermolysis of methylammonium hexachloroplumbate (Fig. 1). With the other compounds, volatilization of the hydrochlorides begins at the first stage and the two processes occur simultaneously, at least over certain temperature ranges.

The differences between the initial temperature of volatilization of the

Temperature [5]		Weight loss (%)						Fig.	Temperature (K) of the phase transition of $[(CH_3)_nNH_{4-n}]Cl$ [10]
of the initial decomposition (K) $T_{\alpha=0.01}$	at which decomposition complete (K) $T_{\alpha=0.99}$	1st stage		2nd stage		total			
		from TG	theoretical [d]	from TG	theoretical [e]	from TG [f]	theoretical [g]		
395	665	16	13.1	31	35.4	47	48.5		
375	615	16	13.1	31	35.4	47	48.5		
460	690								308 (I—II transition) 548 (melting with decomposition)
415	705					51	51.1		
395	700					51	51.1		
520	705								536 (I—II transition)

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[c] w, weak; m, medium; s, strong.

[d] Assuming liberation of one Cl_2 molecule.

[e] Assuming liberation of two molecules of amine hydrochloride.

[f] Based on weight loss at 720 K.

[g] Based on $PbCl_2$ content of the reactants.

appropriate chlorides and the initial temperature of decomposition of the hexachloroplumbate, ΔT, are 40, 115, 100, 65 and 105 K for $(NH_4)_2PbCl_6$, $(CH_3NH_3)_2PbCl_6$, $[(CH_3)_2NH_2]_2PbCl_6$, $[(CH_3)_3NH]_2PbCl_6$ and $[(CH_3)_4N]_2PbCl_6$, respectively. The larger the difference, the more the two processes are separated (see Table 1).

Isothermal experiments (Table 2) showed that the amount of oxidant (chlorine, chloramines etc.) entrained in the gas stream was generally lower than that indicated by eqn. (1). The parameter ν attained higher values for the decomposition of those hexachloroplumbates for which ΔT was large. The amounts of oxidant leaving the reactor decreased with increasing sample mass. In contrast, the values varied only slightly with variation in reaction vessel, decrease in gas flow rate, or increase of temperature. Ammonium and

TABLE 2

Isothermal decomposition data [a]

Reactor [5]	Additional substances [b]	V_{N_2}	$[NH_4]_2PbCl_6$			$[(CH_3)NH_3]_2PbCl_6$			$[(CH_3)_2NH_2]_2PbCl_6$			$[(CH_3)_3NH]_2PbCl_6$			$[(CH_3)_4N]_2PbCl_6$		
			T	m	p	T	m	p	T	m	p	T	m	p	T	m	p
a		300	523	304.6	42	433	301.7	55	433	340.1	57	463	265.8	17	513	300.5	77
				33.0	44		34.4	85		59.7	82		30.2	36		30.9	97
				10.2	49		10.3	98		29.9	96					12.1	97
										12.3	100						
	$PbCl_2$ as layer covering the reactant			33.5	35		34.3	84		31.1	83		32.8	24		31.2	78
	$PbCl_2$ in a mixture with the reactant			34.3	56		33.9	84		30.2	86		33.4	37		30.2	83
	$[(CH_3)_nNH_{4-n}]Cl$ as layer covering the reactant			33.7	37		32.8	84		30.0	66		33.3	6		33.7	72
	$[(CH_3)_nNH_{4-n}]Cl$ in a mixture with the reactant			34.5	34		32.0	81		34.1	63		34.2	7		33.4	46
		20		29.3	30		30.5	89		300.0	57		30.0	20		298.4	53
										39.8	78					29.3	79
										15.3	98					12.1	97
b		300								210.4	51					308.8	88
										35.2	76					37.1	94
a									533	308.2	54				613	310.6	43

[a] V_{N_2}, Nitrogen flow rate through the reactor (cm^3 min^{-1}). T, temperature of thermolysis (K), which was adjusted so that thermal decomposition was completed within 2 h. The decomposition was considered to be complete when oxidant was no longer detected in the gas stream leaving the reactor. The thermolysis temperature usually corresponded to that at which the first endothermic peaks appeared on the DTA curves. m, sample weight (mg). p, 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 added in quantities of ca. 500 mg.

methylammonium chlorides added to reagent mixtures separately or in mixtures slightly decreased the amount of oxidant leaving the reactor. A similar effect was observed in the presence of an inert compound ($PbCl_2$) in the reaction medium. All these facts indicate that chlorine liberated in reaction (1) promotes secondary processes which are likely to occur in the gas phase as indicated by the results of the present work and in the literature. Both ammonia and primary and secondary amines can easily be chlorinated [20, 21]:

$$3\,Cl_2 + 8\,NH_3 \rightarrow 6\,NH_4Cl + N_2 \qquad \Delta H^0_{298} = -77.43\ \text{kJ mole}^{-1} \tag{4}$$

$$CH_3NH_2 + Cl_2 \rightarrow CH_3NHCl + HCl \tag{5}$$

Chloramines, such as CH_3NHCl, are unstable and undergo rapid transformation.

Reactions such as (4) and (5) are responsible for the consumption of chlorine during thermolysis. It is worth noting that reaction (4) has frequently been suggested as the explanation for thermolysis of a variety of ammonium salts of the type $(NH_4)_2MCl_6$, where M = Tc [23], Pd [23], or Ir [24].

Chlorine generated in reaction (1) is a strong oxidant and electron acceptor [25]; hence it should be more reactive towards unprotonated amines compared to the corresponding ammonium cations [26], because the latter are also electron acceptors. The chlorination rate will be dependent on the concentrations of chlorine and the appropriate amine in the gas phase. If reaction (1) occurs at a much lower temperature than reaction (2) (large ΔT), chlorine is almost completely removed from the reaction medium before it can react with the amine. The lower the ΔT value, the higher is the partial pressure of amine in the gas phase during generation of chlorine and the higher the consumption of this oxidant. This is the main reason for the differences in behaviour of individual hexachloroplumbates during thermolysis.

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