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THERMAL REACTIONS OF LEAD(IV) CHLORIDE COMPLEXES IN THE SOLID STATE. PART I. THERMOLYSIS OF HEXACHLOROPLUMBATES AND MOLECULAR COMPLEXES OF $PbCl_4$ WITH PYRIDINE, QUINOLINE AND ISOQUINOLINE

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ABSTRACT

The thermal decomposition of hexachloroplumbic acid salts and of $PbCl_4$ complexes of pyridine, quinoline and isoquinoline has been investigated by thermogravimetry and differential thermal analysis. The decomposition has also been studied isothermally in a device allowing the analysis of both solid and volatile decomposition products. The products of all thermal reactions comprised $PbCl_2$, chlorine, appropriate aromatic bases, their hydrochlorides, chlorinated bases, and other compounds. The influence of sample weight, temperature, rate of removal of volatile products and the effect of certain substances on the course of the thermolysis has also been studied.

INTRODUCTION

Lead(IV) chloride is known to be a strong electron-acceptor [1]. A variety of $PbCl_4$ adducts with electron-donors have been reported, and these can be divided into two groups. The first includes compounds of the general formula $2\ B \cdot PbCl_4$, where B represents an aromatic base [1—3], amide [4] or another compound [1]. To the second group belong alkali metal hexachloroplumbates [1], M_2PbCl_6 with M = K, Rb, Cs; salts of heterocyclic nitrogen-containing aromatic bases [1], $(BH)_2PbCl_6$; amides, $A_4 \cdot H_2PbCl_6$ with A = *N,N*-dimethylformamide [5], and related compounds.

Reports on the thermal reactions of the $PbCl_4$ complexes in the solid state are scant and fragmentary [1,4,6]. The reactions have not been systematically studied so far, and no reports on the thermal analysis of the $PbCl_4$ compounds have been made.

There are, however, some reports on the thermolysis of bi-, tri- and tetravalent metal halide adducts of heterocyclic aromatic bases [7—9] and of the $(C_5H_5NH)_2MCl_6$ salts with M = Ce, Th and Zr [10]. Heating these compounds results in a gradual loss of the free bases. Appropriate metal halides either remain in the residue [7], volatilize [8], or undergo further transformations [10].

Preliminary investigations of the thermolysis of the $PbCl_4$ complexes revealed that their decomposition pattern is unlike that observed with other compounds of this type. The main feature of the decomposition is the release of chlorine due to reduction of lead(IV) to lead(II). This fact makes it possible to initiate a variety of secondary reactions including chlorination of the ligand molecules.

We have decided to study this interesting and complex topic. In this work, we present the results of a study of the thermolysis of the H_2PbCl_6 salts and $PbCl_4$ complexes of simple aromatic bases, pyridine, Py, quinoline, Qu, and isoquinoline, iso-Qu.

EXPERIMENTAL

Analytical grade reagents have been used throughout. Pyridine was purified as described previously [11]. Quinoline and isoquinoline were doubly distilled under reduced pressure.

Hexachloroplumbic acid was prepared by saturation of a suspension of $PbCl_2$ in hydrochloric acid with chlorine gas [1]. The hexachloroplumbates were obtained by treating hexachloroplumbic acid solutions with a small excess of appropriate base hydrochlorides in hydrochloric acid [1]. The compounds were isolated, dried and analysed for Pb(II) and Pb(IV). The results showed that the salts, eg. $(PyH)_2PbCl_6$ were more than 98 mole percent pure. The compounds were stable and could be stored undecomposed for a few months.

Triethylamine hexachloroplumbate was obtained in a similar manner. This compound, added in small portions to a cooled 15% oleum, underwent decomposition to give liquid $PbCl_4$ [2]. Appropriate molecular complexes of $PbCl_4$ were prepared by mixing together cold CCl_4 solutions of the aromatic bases and $PbCl_4$ [2,3]. Results of analyses showed the adducts, e.g. $2\,Py \cdot PbCl_4$ to be more than 96 mole percent pure. The adducts were markedly less stable than the hexachloroplumbates. Even in a vacuum desiccator they could be stored for less than one month.

Hydrochlorides of the aromatic bases ($B \cdot HCl$) were prepared by saturation of ethereal solutions of the bases with HCl gas. The compounds were dried and kept in a vacuum desiccator over P_2O_5 and NaOH owing to their strong hygroscopicity.

Thermal analyses were run on an OD-103 (Monikon) derivatograph. Simultaneously, the thermal decomposition was studied under isothermal conditions in a quartz reactor (Fig. 1). Reactor b was designed to enable the gas stream to pick up volatile products and to cool them rapidly down to room temperature. Samples of compounds to be thermolysed were placed in the reactor immersed in Wood's alloy which had been previously heated to a predetermined temperature. A stream of inert gas (N_2 or Ar) was passed just above the bottom of the reactor to pick up volatile products. The outlet of the reactor was connected in series with absorbers of the products and with a flow meter. In some instances organic solvents were used as absorbing liquids. To determine the quantities of chlorine in the gas stream, the absorbers were filled with acidified KI solutions. Basic compounds, such as aromatic bases and their transformation products, were trapped in an acidified sodium sulphite solution. Following alkalization, the products were

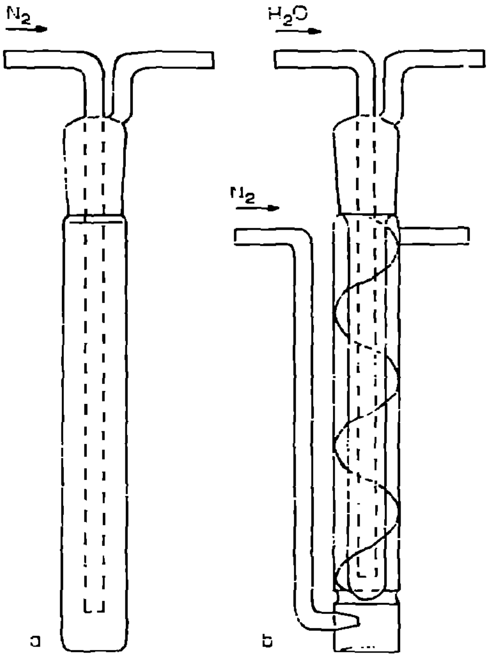

Fig. 1. Quartz reactors.

extracted with ether. The residue left in the reactor was treated with a 5% Na_2CO_3 solution and extracted with ether. Both extracts were analysed by GLC. When solid or liquid products condensed on cold parts of the reactor, they were collected and analysed separately.

Both the reactants and products were analysed as follows: lead(II) was determined complexometrically by titration with a standardised di-Na EDTA solution. Chloride ions were assayed by titration with a $Hg_2(NO_3)_2$ solution, the end point being detected potentiometrically. Lead(IV) and chlorine were assayed iodometrically.

The IR spectra were recorded on a Specord 71 IR spectrophotometer. The UV spectra were taken on a Perkin-Elmer Model 402 and a Specord UV-VIS instrument. The GLC analyses were run on a Pye Unicam Model 104 gas chromatograph equipped with a flame ionization detector. The following column packings were used: 10% PEG 20M on Diatomite C-AW, 10% PEG 6000 on Celite, and 10% Ukon LB 550 on Celite A/W alkalized with a 2% KOH solution.

RESULTS

The DTA, TG and DTG curves for the H_2PbCl_6 salts and $PbCl_4$ adducts with simple aromatic bases show that their thermal decomposition is not preceded by melting, and that the process is complex. Relevant data shown in Figs. 2 and 3 and in Table 1 allow the following observation: in all runs loss in weight was observed upon heating. However, no well-defined decomposition steps could be discerned in the TG and DTG curves, thus indicating

TABLE 1

The thermal analyses were made with a derivatograph in a dynamic atmosphere of nitrogen or air. α-Al_2O_3 served as a reference. The sensitivities of the galvanometer were 1/5 and 1/20 for DTA and DTG curves respectively.

Substance	Sample weight (mg)	Sample holders[a]	Heating rate (K min^{-1})	Temperatures and character of peaks in DTA[b]		Temperatures [12]		Percent weight loss		Figures
				Exothermic (K)	Endothermic (K)	At the beginning of decomposition $T_{\alpha=0.01}$ (K)	At the end of decomposition $T_{\alpha=0.99}$ (K)	TG[c]	Theoretical[d]	
$(PyH)_2PbCl_6$	800	C	5		495s, 545s, 560w, 580m (unresolved)	425	590	52	52.1	2a
$(PyH)_2PbCl_6$	800	P	5		455s, 490m, 510s (unresolved)	385	530	52	52.1	2c
2 Py · HCl + $PbCl_2$	703	C	5		510w, 545s, 580m (unresolved)	380	600			2b
2 Py · $PbCl_4$	800	C	2.5	425s (sharp)	520m, 540m, 565w (unresolved)	385		44	45.2	3a
2 Py · $PbCl_4$	160	C(Pt)	2.5		415m, 490m	330		46	45.2	3b
$(QuH)_2PbCl_6$	600	C	5		450m, 555m, 590m (unresolved)	415	600	59	59.1	
$(QuH)_2PbCl_6$	600	P	5		440m, 485m, 525s	380	590	59	59.1	
2 Qu · HCl + $PbCl_2$	537	C	5		425m (melting) 560w, 580w, 595m (unresolved)	455	600			
2 Qu · $PbCl_4$	350	C	5	340w, 370w, 395w (unresolved)	445w, 565w, 580w (unresolved)	340		46	54.2	

TABLE 1 (continued)

Substance	Sample weight (mg)	Sample holders [a]	Heating rate (K min^{-1})	Temperatures and character of peaks in DTA [b]		Temperatures [12]		Percent weight loss		Figures
				Exothermic (K)	Endothermic (K)	At the beginning of decomposition $T_{\alpha=0.01}$ (K)	At the end of decomposition $T_{\alpha=0.99}$ (K)	TG [c]	Theoretical [d]	
2 Qu · $PbCl_4$	350	P	5		380w, 445w, 505w (unresolved)	340		47	54.2	
$(iso\text{-}QuH)_2PbCl_6$	600	C	5		380s, 445w, 585w, 605w, (unresolved)	345	620	59	59.1	
$(iso\text{-}QuH)_2PbCl_6$	600	P	5		350s, 425m, 505s, 600w (unresolved)	330	600	59	59.1	
2 iso-Qu · HCl + $PbCl_2$	637	C	5		420m (melting) 585w, 610m (unresolved)	450	610			
2 iso-Qu · $PbCl_4$	350	C	5	390s	480w, 570w (unresolved)	330		40	54.2	
2 iso-Qu · $PbCl_4$	350	P	5	390s	465w, 505w (unresolved)	330		42	54.2	

[a] C = ceramic crucible, C(Pt) = platinum crucible, P = five platinum plates.

[b] w = weak, m = medium, s = strong.

[c] Based on the weight loss in 720 K.

[d] Based on $PbCl_2$ content in the reactants.

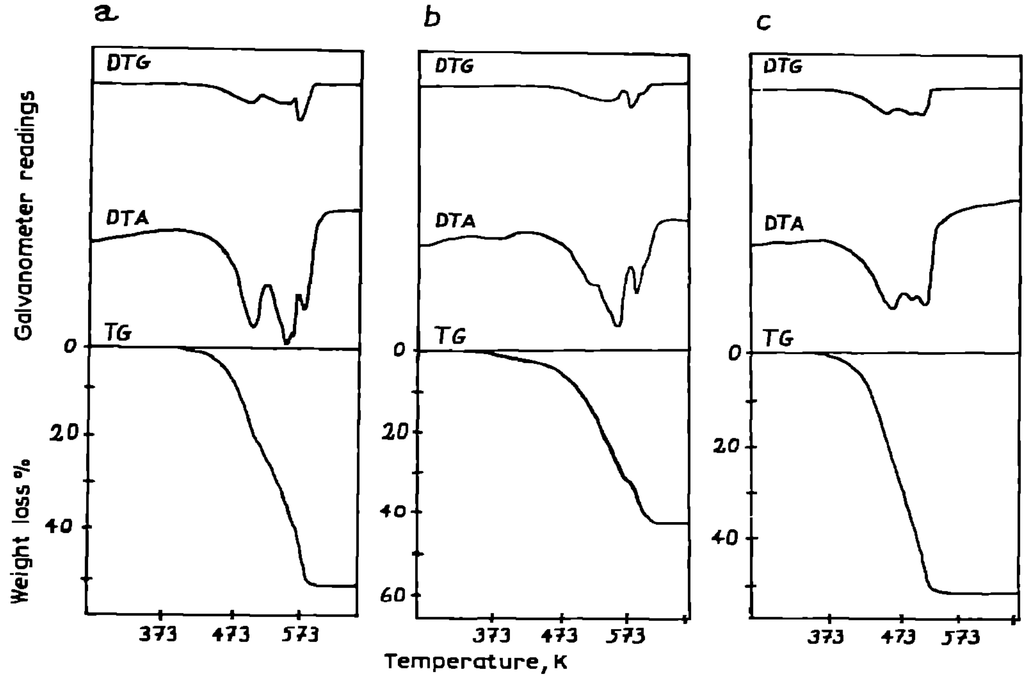

Fig. 2. Thermal analysis of $(PyH)_2PbCl_6$ (cf. Table 1).

a number of concurrent processes. The residue was white or grey with hexachloroplumbates and dark-grey or even brown with the molecular complexes. In the case of the hexachloroplumbates the composition of the residue corresponded almost exactly to that of $PbCl_2$, as demonstrated by

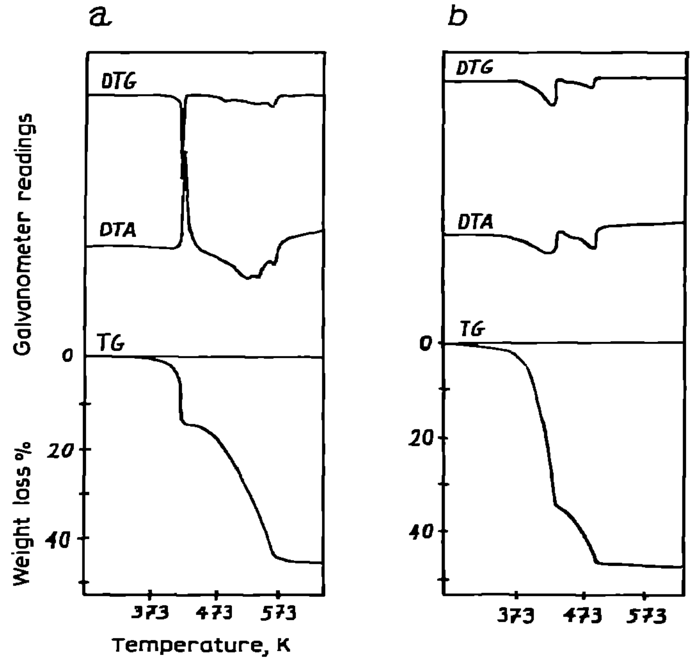

Fig. 3. Thermal analysis of 2 Py · $PbCl_4$ (cf. Table 1).

the results of analyses and TG data. The grey colour suggests contamination of $PbCl_2$ with carbonization products. The weight of the residue for molecular complexes was much greater than that expected for $PbCl_2$.

The DTA curves show that the thermal decomposition of hexachloroplumbates is endothermic. The first endothermic peaks appear at high temperatures for pyridine hexachloroplumbate and at lower temperatures for quinoline and isoquinoline hexachloroplumbates. The same sequence has been noted for the decomposition temperatures ($T_{\alpha=0.01}$) [12] of the hexachloroplumbates. A comparison of the DTA curves of hexachloroplumbates with those of 2 : 1 (mole ratio) mixtures of the base hydrochlorides with $PbCl_2$ revealed that further endothermic peaks were identical in shape and occurred at the same temperatures. The low-temperature endothermic peaks observed in the DTA curves of the mixtures corresponds to melting of the hydrochlorides. However, the melting points are lower than the temperatures corresponding to the first endothermic DTA peaks of the hexachloroplumbates.

The thermal decomposition of the molecular complexes of $PbCl_4$ is largely dependent on the conditions of thermal analysis. If the runs were performed with large samples in a ceramic crucible, exothermic peaks always appeared first in the DTA curves. The peak for the pyridine complex was sharp, while those for the remaining compounds were small and unresolved. On the other hand, when the same mass was placed on five platinum plates, a different result was observed. An identical exothermic peak was observed for quinoline, while that due to the isoquinoline complex did not appear at all. An endothermic DTA peak for the pyridine complex was observed in its place (Fig. 3).

It is worth noting that for the pyridine complex only, the temperatures corresponding to the first endo- or exothermic peaks are higher than its boiling point (388.7 K). The decomposition of the two remaining compounds begins well below the boiling points (511 and 516 K for quinoline and isoquinoline, respectively).

The decomposition temperatures ($T_{\alpha=0.01}$) were usually lower for the molecular complexes than for the corresponding hexachloroplumbates. This was also true for the temperatures corresponding to the first DTA peaks.

The furnace atmosphere (N_2 or air) did not affect the results of the analyses.

Additional information could be obtained from decomposition runs in an assembly allowing qualitative (and occasionally also quantitative) evaluation of the products. The results have been listed in Tables 2 and 3, and lead to the following conclusions. The quantity of chlorine liberated and carried off the reactor is usually smaller than that corresponding to the Pb(IV) content of a compound. The quantity liberated (mole percent, cf. Table 2) depends on a variety of factors. The quantity of chlorine carried off the reactor during the decomposition of the hexachloroplumbates is larger than that produced during the decomposition of the corresponding molecular complexes. Within a particular group of compounds, the quantities are largest for pyridine and smaller for the two remaining bases, generally being higher for isoquinoline than for quinoline. The ϑ values decrease as the weight of the

TABLE 2

Isothermal decomposition data

Additional substances	Reactor	Substance and thermolysis parameters [a]										
		$(PyH)_2PbCl_6$				$2\,Py \cdot PbCl_4$			$(QuH)_2PbCl_6$			
		V_{N_2}	T	m	ϑ	T	m	ϑ	V_{N_2}	T	m	ϑ
	b	200	485	804.1	98	405	936.8	58				
	a			803.1	95		802.6	44	100	445	602.2	22
				33.2	100		30.6	91			64.3	63
							14.8	100			9.8	79
		30		809.8	91		34.3	81	5		65.4	26
$PbCl_2$												
The layer covering the reactant		200		32.7	92		33.2	91	100		60.2	42
		30					33.2	90				
In a mixture with the reactant		200		35.2	100		33.0	96			61.3	79
		30					31.9	95				
$B \cdot HCl$												
The layer covering the reactant		200		33.7	6.0						61.1	—
In a mixture with the reactant				31.3	6.7						60.6	1.3
			575	805.7	92	505	800.0	16				

TABLE 2 (continued)

Additional substances	Reactor	Substance and thermolysis parameters [a]								
		2 Qu · $PbCl_4$			$(iso\text{-}QuH)_2PbCl_6$			2 iso-Qu · $PbCl_4$		
		T	m	ϑ	T	m	ϑ	T	m	ϑ
	a	445	350	3.0	385	600	30	405	350	9.7
			62.1	16		61.8	65		62.1	13
			36.7	25		9.7	76		35.1	24
			6.0	33					6.0	36
			63.4	8.5		60.1	28		65	6.3
$PbCl_2$										
The layer covering the reactant			60.4	5.5		63.7	43		60.1	8.7
In a mixture with the reactant			61.0	6.3		63.7	76		63.5	10
B · HCl										
The layer covering the reactant						64.5	3.1			
In a mixture with the reactant						65.0	13			

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[a] V_{N_2}, nitrogen flow rate through the reactor (cm^3 min^{-1}). T, temperature of thermolysis (K). This temperature was adjusted when the thermal decomposition was *completed within 2 h*. The decomposition was considered to be complete when chlorine was no longer detected in the gas stream leaving the reactor. The thermolysis temperature usually *corresponded to those at which the first DTA peaks appeared on the DTA* curves. m, sample weight (mg). ϑ, mole percent of liberated chlorine. This magnitude was determined by an analytical ratio of the number of moles of chlorine trapped in the KI absorbers to the number of moles of Pb (IV) in a reactant.

[b] Additional substances were added in quantities of ca. 500 mg.

TABLE 3

Thermal decomposition products

Substances	Temperature (K)	Sample weight (mg)	Thermolysis products [a]		
			Remaining in the reactor		Carried off the reactor
			On the bottom (colour of residue)	Condensed on cold walls of the reactor	
$(PyH)_2PbCl_6$	485	30 [b]	$PbCl_2$ (white) [c]	Py · HCl [d]	Cl_2 [e]
		800	$PbCl_2$ [c] (light-yellow)	Py · HCl [d]	Cl_2 [e], Py [f], 3-ClC_5H_4N [f], 2-ClC_5H_4N [f], 3,5-$Cl_2C_5H_3N$ [f], other compounds [f]
2 Py · $PbCl_4$	405	15 [b]	$PbCl_2$ [c] (white)		Cl_2 [e], Py [g]
		800	$PbCl_2$ [c] (grey)	Py · HCl [d]	Cl_2 [e], Py [f], 3-ClC_5H_4N [f], 4-ClC_5H_4N [f], 3,5-$Cl_2C_5H_3N$ [f], other compounds [f]
			Py [h], 3-ClC_5H_4N [h], 3,5-$Cl_2C_5H_3N$ [h], other compounds [h]		
$(QuH)_2PbCl_6$	445	60	$PbCl_2$ (grey) [c]	Qu · HCl [d]	Cl_2 [e]
			Qu [h], other compounds [h]		

2 Qu · $PbCl_4$	445	60	$PbCl_2$ [c] (dark-grey)	Qu · HCl [d], Qu [i]	Cl_2 [e]
			Qu [h], other compounds [h]		
$(iso\text{-}QuH)_2PbCl_6$	385	60	$PbCl_2$ [c] (grey)	iso-Qu · HCl [d]	Cl_2 [e]
			iso-Qu [h], other compounds [h]		
2 iso-Qu · $PbCl_4$	405	60	$PbCl_2$ [c] (dark-grey)	iso-Qu · HCl [d] iso-Qu [i]	Cl_2 [e]
			iso-Qu [h], other compounds [h]		

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[a] Analytical procedures used for the detection and determination of products have been given as superscripts.

[b] Products formed in stoichiometric quantities.

[c] Complexometric (Pb(II)) and mercurimetric (Cl^-) assays.

[d] UV and IR spectral analysis of the residues and of authentic samples, also based on mercurimetric Cl^- assays.

[e] Analysis of the UV spectra of solutions left after passing inert gas stream through CCl_4, also based on iodometric determinations.

[f] GLC assay of ethereal extracts from absorbers.

[g] Pyridine was assayed spectrophotometrically after extraction into CCl_4 from the gas stream.

[h] GLC assay of ethereal extracts from the reactor.

[i] UV and GLC assay of a liquid condensed at the bottom of the reactor, below the layer of the precipitate of a base hydrochloride.

sample subjected to thermolysis increases. With sufficiently small samples of pyridine hexachloroplumbate and its molecular complex, stoichiometric quantities of chlorine are determined in each case. An increase in the flow rate of the inert gas increases the ϑ values. On the other hand, raising the temperature usually reduces the ϑ values. Rapid removal and cooling of volatile products (cf. data for reactors a and b) increases the quantity of chlorine carried off the reactors.

When the thermolysis of the hexachloroplumbates was carried out in the presence of the hydrochlorides of the corresponding bases, a considerable decrease in the ϑ values was noted, compared with the values found for pure hexachloroplumbates. The values were found to be higher during thermal decomposition of the mixtures than during decomposition of a hexachloroplumbate covered with a layer of appropriate base hydrochloride.

Yet another result was observed during thermal decomposition carried out in the presence of an inert component ($PbCl_2$). In this case, the quantity of chlorine carried off the reactor was generally larger than in the absence of $PbCl_2$. However, ϑ values lower than for pure hexachloroplumbates were obtained when the compound was covered with a layer of $PbCl_2$.

In all cases, chlorine and $PbCl_2$ provide thermal reaction products (Table 3). The latter is white to dark-grey in colour. The dark-grey colour is due to the presence of non-volatile substances such as carbonized products. Other products detected were aromatic base hydrochlorides. These are always present among the thermolysis products of hexachloroplumbates, and occasionally, of molecular complexes as well. On the other hand, thermolysis of the molecular complexes always gives aromatic bases; chlorinated bases were also present and, with pyridine, were carried off the reactor. The yield of the chlorination products were inversely dependent on the ϑ values. Not all of the products could be isolated by the methods employed; not all of the compounds isolated could be identified.

Thermal decompositions of small samples of pyridine compounds were such that the reactants and simple products could be balanced.

DISCUSSION

Both the hexachloroplumbates and molecular complexes of $PbCl_4$ with the aromatic bases studied undergo decomposition upon heating up to 750 K. In simple cases, the thermal reaction may be described by the following equations:

for hexachloroplumbates

$$(BH)_2PbCl_6 \rightarrow PbCl_2 + Cl_2 + 2\,(B \cdot HCl) \qquad (1)$$

for molecular complexes

$$2\,B \cdot PbCl_4 \rightarrow PbCl_2 + Cl_2 + 2\,B \qquad (2)$$

These may be considered as primary reactions for all the compounds studied. $PbCl_2$ was quite stable up to 750 K, as demonstrated by the thermal studies. It may therefore be assumed that $PbCl_2$ does not participate in further transformations. Compounds of the type 2 B · $PbCl_2$ have been described [13], but they are as unstable as those studied here. If such compounds had been formed, reaction (2) would occur in two steps. This, however, has been ruled out by the results of the thermal analyses (Fig. 3). Interactions between $PbCl_2$ and base hydrochlorides are improbable.

It is difficult to establish whether decomposition of the compounds is accompanied by the loss of molecular or atomic chlorine. However, chlorine should pass to the gas phase, irrespective of the mechanism of the decomposition.

The same reasoning suggests that base hydrochlorides formed in reaction (1) appear as liquids. This is supported both by literature data (m.p. of Py · HCl and Qu · HCl are 355 and 407.5 K, respectively [14]) and by the data listed in Table 1. As far as the form of the bases released in reaction (2) is concerned, quinoline and isoquinoline may appear preferentially as liquids, while pyridine should pass into the gas phase.

Mechanisms of heat conduction suggest that the thermal decomposition of the compounds begins in the external layers of crystals or molecular clusters [15]. When the decomposition of 2 Py · $PbCl_4$ is accomplished in a thin layer (in a crucible or a quartz reactor), volatile products diffuse readily into the gas phase and can thus be quickly removed from the reaction site. The decomposition inside a crystal proceeds in a similar manner, but the diffusion of products can be slightly hampered due to the formation of a $PbCl_2$ layer. Stoichiometric quantities of volatile products were actually removed during the thermolysis of small 2 Py · $PbCl_2$ samples (Tables 2 and 3). In cases where the removal of the products is hindered (for instance, with large samples, slower gas-flow rate, lower temperature, presence of a $PbCl_2$ layer covering the compound, etc.), analytically-assayed quantities of chlorine are smaller than the stoichiometric values. The diffusion of chlorine is impeded still further when bases or their hydrochlorides appear as liquids during the decomposition.

Smaller quantities of chlorine than expected indicate secondary processes leading to chlorinated aromatic bases, among other products (Table 3). Equations describing those processes can be written as follows (taking a molecular complex of pyridine as an example):

$$C_5H_5N + Cl_2 \rightarrow 2\text{-}ClC_5H_4N + HCl \tag{3}$$

$$\rightarrow 3\text{-}Cl_5H_4N + HCl \tag{4}$$

$$C_5H_5N + 2\,Cl_2 \rightarrow 3{,}5\text{-}Cl_2C_5H_3N + 2\,HCl \tag{5}$$

$$\rightarrow \text{other products} \tag{6}$$

$$C_5H_5N + HCl \rightarrow C_5H_5N \cdot HCl \tag{7}$$

Secondary reactions may occur between chlorine gas and solid reagents. It is difficult to estimate the contribution of these reactions to the overall process. However, it follows from the general nature of phase-boundary controlled reactions that the contribution should be small. On the other hand, chlorination of aromatic bases is known to be catalysed by Lewis acids owing to the formation of compounds resembling 2 B · $PbCl_4$ [16,17]. It seems likely that the secondary reactions include those between Cl_2 and aromatic bases or their hydrochlorides formed in the liquid or gas phases.

Chlorination of nitrogen-containing aromatic bases has been extensively studied [17]. However, the reactions have not been elucidated completely, due to the complexity of the process. Chlorination of liquid pyridine occurs very quickly, a pyridyl-pyridinium chloride presumably providing an intermediate product [11]. Mostly isomeric mono- and dichloropyridines are formed in the gas phase [18,19]. Chlorination of liquid quinoline in the temperature range 430—460 K gives rise to a mixture of products, including some isomers of di-, tri-, tetra- and pentachloroquinolines [20]. These findings have been supported in many instances by our results. The complexity of the chlorination processes taking place during thermolysis of the molecular complexes has been indicated by the course of the DTA and DTG curves and by the residue having a weight much higher than that expected for $PbCl_2$.

The problem of chlorination of the hydrochlorides of the bases can be discussed in terms of electrophilic substitution [16,17,21]. Halogenation processes of cations are more selective and usually afford simpler products than does halogenation of the free bases. For instance, chlorination of pyridine in sulphuric acid at 400 K gave 3-chloropyridine as the main product [17]. Bromination of the hydrochlorides of quinoline and isoquinoline in nitrobenzene gave 3-bromoquinoline and 4-bromoisoquinoline, respectively [22].

In our experiments, liquid base hydrochlorides should initially undergo chlorination (cf. Table 2 for the effect of B · HCl on the course of the thermolysis). Equations describing these reactions are as follows (taking pyridine hexachloroplumbate as an example):

$$C_5H_5N \cdot HCl + Cl_2 \rightarrow 1\text{-}ClC_5H_4N \cdot HCl + HCl \quad (8)$$

$$\rightarrow 2\text{-}ClC_5H_4N \cdot HCl + HCl \quad (9)$$

$$C_5H_5N \cdot HCl + 2\ Cl_2 \rightarrow 3,5\text{-}Cl_2C_5H_3N \cdot HCl + 2\ HCl \quad (10)$$

$$\rightarrow \text{other products} \quad (11)$$

Liquid $PbCl_4$ is known to be thermodynamically unstable. The enthalpy of its decomposition to $PbCl_2$ and Cl_2 amounts to ca. 6 kJ mole^{-1} [1]. On the other hand, the $PbCl_6^{2-}$ anion is quite stable [1]. The energies of the two compounds become lower upon attachment of the free bases or their cations to form crystalline phases. The effect is usually more pronounced in the latter case. It therefore seems likely that hexachloroplumbates are more thermodynamically stable than the corresponding complexes. This has been fully confirmed by the results of our measurements.

A comparison of the relative stability of the compounds of both groups was difficult. The values of the dissociation constants of the bases are comparable [23], and the stabilities of these compounds should therefore be similar. However, it seems likely that the stability of these compounds is determined not only by the basicity of the bases, but also by the ease with which they undergo chlorination. Quinoline and isoquinoline undergo chlorination more readily than pyridine owing to the enhanced reactivity of the carbocyclic ring [21,24]. During thermolysis of the quinoline and isoquinoline compounds, a contribution due to intramolecular chlorination must also be considered. The contribution to the overall reaction appears to be small. Were it larger, the results of thermal analyses would be independent of the sample weights. However, reactions such as intramolecular chlorination can accelerate the decomposition, i.e. decrease the thermal stability of the compounds.

Chlorination reactions are exothermic, as indicated by a comparison of the energies of the bonds being cleaved and the new bonds being formed during chlorination. Corresponding exothermic DTA peaks should therefore appear, and this effect is actually observed with large and compact samples of the molecular complexes. With smaller samples, or for those compounds being decomposed in thin layers, the contribution of the chlorination reactions is smaller and occurs partly in the gas phase. The associated energetic effect does not balance losses due to the simultaneous decomposition of the compounds (endothermic effect). The same reasons are responsible for the absence of exothermic peaks with hexachloroplumbates.

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