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THERMAL REACTIONS OF LEAD(IV) CHLORIDE COMPLEXES IN THE SOLID STATE. PART II. THERMOLYSIS OF MOLECULAR COMPLEXES OF $PbCl_4$ AND H_2PbCl_6 WITH *N,N*-DIMETHYLFORMAMIDE AND *N,N*-DIMETHYLACETAMIDE

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ABSTRACT

The following molecular complexes of $PbCl_4$ and H_2PbCl_6 with *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) are obtained: $PbCl_4 \cdot 2$ DMF, $PbCl_4 \cdot 2$ DMA, $H_2PbCl_2 \cdot n$ DMF and $H_2PbCl_6 \cdot n$ DMA. The thermal decomposition of these compounds is studied both by thermal analysis, and isothermally in a device to separate reaction products. The products of thermal reactions are $PbCl_2$, Cl_2, HCl, and appropriate amides or their hydrochlorides. In addition, a variety of products of secondary reaction, including those of pyrolysis of the amides (amines, CO, CO_2 and nitriles) and chlorination (e.g. $COCl_2$) are detected. The effect of sample weight, temperature, rate of removal of volatile products, and presence of certain substances on the course of the thermolysis is also investigated. An attempt is made to elucidate the thermal processes taking place during the decomposition.

INTRODUCTION

Carboxylic acid amides are Lewis bases [1—10]. The basic nature of these compounds has been ascribed mainly to the presence of lone electron pairs at the oxygen atom [1—8] rather than at the nitrogen atom [7,9,10]. In the group of basic (electron-donor) organic compounds, amides occupy an intermediate position between aromatic bases, which are known as strong *n*-electron donors, and aromatic hydrocarbons which are much weaker π-electron donors [11].

The objective of this work was to extend our studies on the properties of solid complexes of $PbCl_4$ and hexachloroplumbic acid [12] by including their adducts with simple amides, *N,N*-dimethylformamide and *N,N*-dimethylacetamide. These amides are known to form a variety of adducts [2,9—11, 13—18] and salt-like compounds [1,4,5,19]. However, appropriate compounds of $PbCl_4$ have received only scant attention; the compound $H_2PbCl_6 \cdot 4$ DMF has been reported by Frydrych [19] and we prepared the adduct $PbCl_4 \cdot 2$ DMF [11]. Analogous adducts with DMA have not been reported so far. Some DMF and DMA complexes have been studied by thermal analysis [9,10,13—16], and the thermolysis of $PbCl_4 \cdot 2$ DMF has been reported earlier [11]. In this paper the results of our studies on the preparation, properties and thermolysis of the $PbCl_4$ and H_2PbCl_6 complexes with DMF and DMA will be described.

EXPERIMENTAL

Analytical grade reagents were used throughout. DMF and DMA were dried over $MgSO_4$ and doubly distilled under reduced pressure.

Hexachloroplumbic acid, $PbCl_4$ and the amide adducts of $PbCl_4$ were prepared by a method described earlier [11,12]. The H_2PbCl_6 adducts of the amides were prepared by reacting the acid with a 20—40-fold excess of the amide in solution. Hexachloroplumbic acid was found to form adducts with a variable number of amide molecules: $H_2PbCl_6 \cdot n$ DMF and $H_2PbCl_6 \cdot n$ DMA. From among a variety of compounds prepared in this work $H_2PbCl_6 \cdot 3$ DMF and $H_2PbCl_6 \cdot 4$ DMA were selected for thermal investigations. The products were filtered off, dried and analysed for total lead and Pb(IV); the results showed that $PbCl_4 \cdot 2$ DMF, $PbCl_4 \cdot 2$ DMA, $H_2PbCl_6 \cdot 3$ DMF and $H_2PbCl_6 \cdot 4$ DMA adducts to be 97, 100, 100 and 101 mole% pure, respectively. The compounds were kept in a light-protected vacuum desiccator.

The hydrochlorides of the amides were prepared by passing a stream of dry HCl through amide solutions in absolute ether [4,5]. Picrates of aliphatic amines were obtained by saturation of picric acid solutions in absolute ethanol with a stream of the appropriate amine in nitrogen.

The thermal analyses were done on an OD-103 derivatograph (Monikon) with α-Al_2O_3 as reference, in a dynamic atmosphere of nitrogen or air. The sensitivities of the galvanometer were 1/5 and 1/20 for the DTA and DTG curves, respectively. The samples were placed in a ceramic crucible (C), or on five platinum plates (5P), or on one platinum plate (P). The theoretical weight loss (t) was calculated on the $PbCl_2$ content in the reactants.

The isothermal measurements were carried out by the procedure previously described [12]. Amine products were identified by GLC and additionally by absorbing them in ethanolic solutions of picric acid; the corresponding picrates were then identified by taking their IR and ^{1}H-NMR spectra. Carbon monoxide was detected with $PdCl_2$ solution [20]. Phosgene and nitriles were detected by indicators designed for detection of gases in warfare. Carbon dioxide was identified by absorbtion in $Ba(OH)_2$ solution.

The analytical methods used were as previously described [12]. GLC analyses were run with columns packed with Chromosorb 103 (100—120 mesh) or 28% Pennwalt 223 + 4% KOH on Gas-Chrom R (80—140 mesh). The ^{1}H-NMR spectra were recorded on a Tesla BS 487 C spectrometer operated at 80 MHz.

RESULTS AND DISCUSSION

Both DMF and DMA form stable adducts with $PbCl_4$ and chloroplumbic acid. The composition of these adducts, determined by their lead content and results of thermal analyses, is as follows: $PbCl_4 \cdot 2$ DMF [11], $PbCl_4 \cdot 2$ DMA, $H_2PbCl_6 \cdot n$ DMF [19] and $H_2PbCl_6 \cdot n$ DMA, with $n = 2$–4.

As has already been noted, the electron-donating nature of these amides is mainly due to the carbonyl oxygen [1—8,11]. Coordination through the oxygen atom manifests itself in a shift of the C=O band in the IR spectrum towards lower frequencies [2—6,11,18]. This was also observed in the spectra of the adducts obtained in this work where the differences between non-bonded and bonded C=O stretching vibrations were ca. 30 [11], 20, 20, and 10 cm^{-1} for $PbCl_4 \cdot 2$ DMF, $PbCl_4 \cdot 2$ DMA, $H_2PbCl_6 \cdot 3$ DMF and $H_2PbCl_6 \cdot 4$ DMA, respectively.

The structure of the non-bonded $PbCl_4$ molecule results from sp^3 hybridisation of the lead(IV) atom [11]. Attaching two amide molecules probably results in an octahedral structure because of sp^3d^2 hybridisation [11,16]. In the $PbCl_6^{2-}$ anion the octahedrally hybridised central atom is surrounded by six Cl atoms. Hence, the H_2PbCl_6 adducts are probably formed by hydrogen bonding between the protons of the acid and carbonyl oxygen atoms of the amide molecules, as is the case in other compounds of this type [4,5,6—8]. Further amide molecules are attached owing to interaction with previously bound molecules [2,3,6,17].

The results of thermal analyses are shown in Figs. 1—4 and Table 1 lists the results of isothermal decompositions.

Thermolysis of the $PbCl_4$ complexes was not preceded by melting. In contrast, analogous complexes of H_2PbCl_6 melted on heating, as indicated by the first endothermal DTA peaks (the melting points of $H_2PbCl_6 \cdot 3$ DMF and $H_2PbCl_6 \cdot 4$ DMA were measured as 382 K and 339 K, respectively).

Temperatures corresponding to the initial decomposition of the compounds, $T_{\alpha=0.01}$, and those corresponding to the first DTG and DTA peaks are higher for the hexachloroplumbic acid adducts than for the corre-

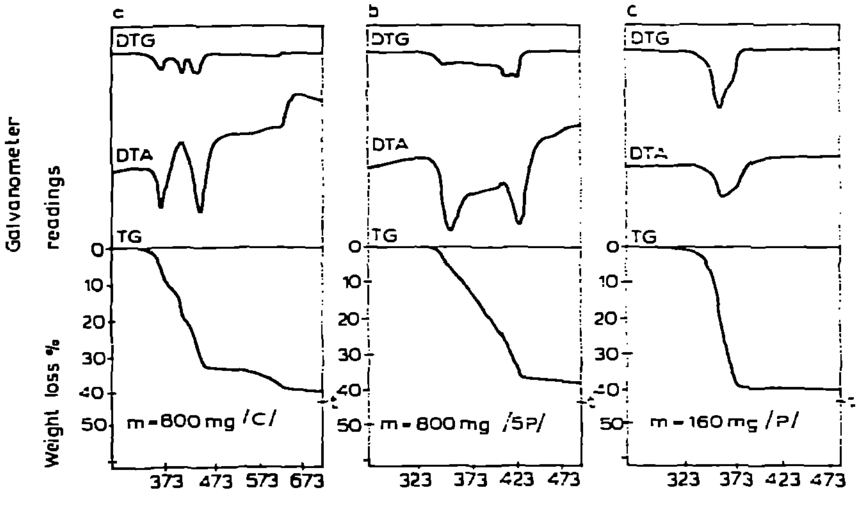

Fig. 1. Thermal analysis of $PbCl_4 \cdot 2$ DMF.

TABLE 1

Isothermal decomposition data [a]

Reactor [12]	Additional substances [b]	V_{N_2}	PbCl$_4$ · 2DMF				PbCl$_4$ · 2DMA			
			T	m	ν	Thermolysis products	T	m	ν	Thermolysis products
a		200	373	30.5	99	PbCl$_2$ [c] 99% of the residue	373	30.8	53	PbCl$_2$ [c] 89% of the residue
				561.7	58			562.1	19	
			443	28.3	100		443	28.1	36	
				555.2	70			547.0	24	
	PbCl$_2$ as a layer covering the reactant		373	28.3	90		373	28.9	43	
			443	29.5	98		443	29.2	31	
	PbCl$_2$ in a mixture with the reactant		373	30.1	87		373	30.7	46	
			443	28.6	93		443	29.8	33	
b			373	29.5	97		373	29.0	54	
				560.2	70			568.8	21	
			443	29.7	98		443	28.0	52	
				562.9	67			557.9	24	
		20	373	30.1	84		373	28.7	32	
				557.2	54			560.6	10	
			443	27.3	78		443	27.2	23	
				547.4	62			555.9	14	
a,b		200	373, 443	550		Cl$_2$ [d] COCl$_2$ [e] RCN [e] CO [f] DMF [h] DMF [i] $(CH_3)_2NH$ [k] $(CH_3)_2NH \cdot HCl$ [11] Others [h,i]	373, 443	550		Cl$_2$ [d] COCl$_2$ [e] RCN [e] CO [f] DMA [h] DMA [i] Others [h,i]

[a] V_{N_2}, Nitrogen flow rate through the reactor (cm^3 min^{-1}). T, Temperature of thermolysis (K). This temperature was adjusted so that the thermal decomposition was completed within 2 h. The decomposition was considered to be complete when oxidant (e.g. chlorine) was no longer detected in the gas stream leaving the reactor. The thermolysis temperatures corresponded usually to those at which the first DTA peaks appeared on the DTA curves. m, sample weight (mg). ν, mole% of liberated oxidants. This value was determined by the analytical ratio of the number of moles of oxidant trapped in the KI absorber to the number of moles of Pb(IV) in the reactants.

[b] Additional substances were added in quantities of ca. 1 g.

[c] Complexometric (Pb(II)) and mercurimetric (Cl$^-$) procedures used for detection and determination of products.

sponding PbCl$_4$ adducts. The residues left after decomposition of the H$_2$PbCl$_6$ adducts corresponded exactly to PbCl$_2$, whereas thermolysis of the PbCl$_4$ complexes give a grey residue containing PbCl$_2$ as the major, but not the sole, component (see Figs. 1—4 and Table 1).

V_{N_2}	$H_2PbCl_6 \cdot 3DMF$				$H_2PbCl_6 \cdot 4DMA$			
	T	m	ν	Thermolysis products	T	m	ν	Thermolysis products
230	393	30.8	94	$PbCl_2$ [c] 100% of the residue	393	30.7	91	$PbCl_2$ [c] 100% of the residue
		597.7	31			598.4	2	
	523	30.9	76		523	30.5	18	
20	393	30.4	50		393	29.7	21	
230		31.2	93			29.2	90	
		31.1	94			29.8	91	
		602.6	34			597.6	9	
	523	596.8	84		523	600.6	6	
230	393, 523	600		Cl_2 [d] CO_2 [g] DMF [h] DMF [i] Others [h,i]	393, 523	600		Cl_2 [d] $COCl_2$ [e] RCN [e] CO_2 [g] DMA [h] DMA [i] $DMA \cdot HCl$ [j] Others [h,i]

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[d] Iodometric procedures used for detection and determination of products.

[e] Indicators for gases in warfare were used for detection and determination of products.

[f] $PdCl_2$ solution [20] used for detection and determination of products.

[g] Saturated aqueous solution of $Ba(OH)_2$ used for detection and determination of products.

[h] GLC assay of ethereal extracts from absorbers [12].

[i] GLC assay of ethereal extracts from the reactor [12].

[j] IR, ^1H-NMR and GLC assay of solid crystals deposited on the cooled part of reactor b [12].

[k] GLC analyses used for detection and determination of products together with IR and ^1H-NMR for appropriate picrates.

By analogy with the results of thermolysis of previously studied [12] $PbCl_4$ and H_2PbCl_6 complexes with aromatic bases, the following primary processes can be suggested for the thermal decomposition of the amide

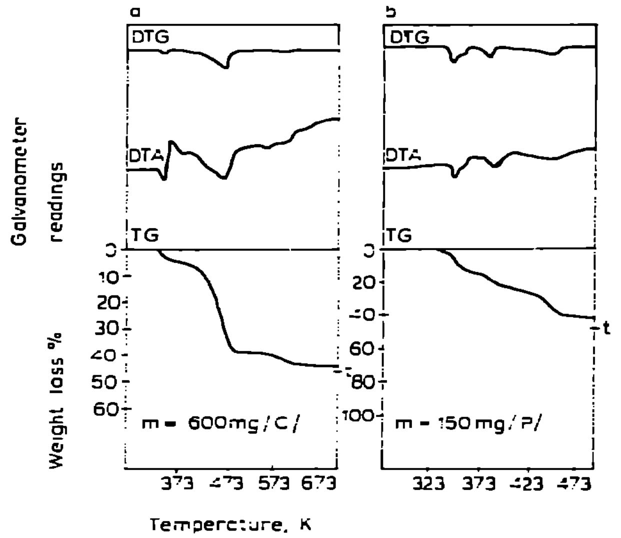

Fig. 2. Thermal analysis of $PbCl_4 \cdot 2$ DMA.

adducts (as illustrated by the DMF compounds):

$$PbCl_4 \cdot 2\,DMF(s) \rightarrow PbCl_2(s) + 2\,DMF(l) + Cl_2(g) \qquad (1)$$

$$H_2PbCl_6 \cdot 3\,DMF(l) \rightarrow PbCl_2(s) + 3\,DMF(l) + 2\,HCl(g)\ (\text{or } DMF \cdot HCl(l)) + Cl_2(g) \qquad (2)$$

The chlorine is volatile, whereas the amides and their hydrochlorides remain in the liquid phase (b.p. of DMF, DMA and m.p. of DMF · HCl and DMA · HCl are 426, 438, 316 [3] and 375 K — our measurements — respectively). When thermolysis was carried out under conditions which facilitated free

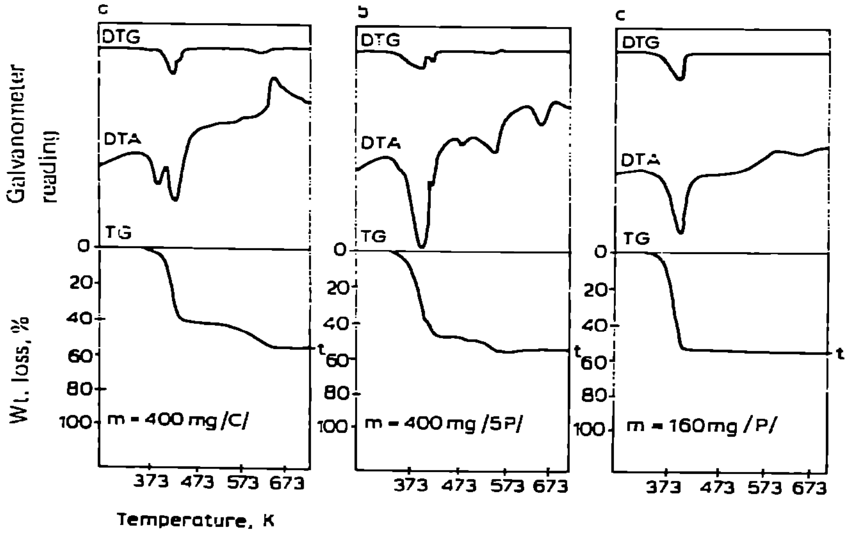

Fig. 3. Thermal analysis of $H_2PbCl_6 \cdot 3$ DMF.

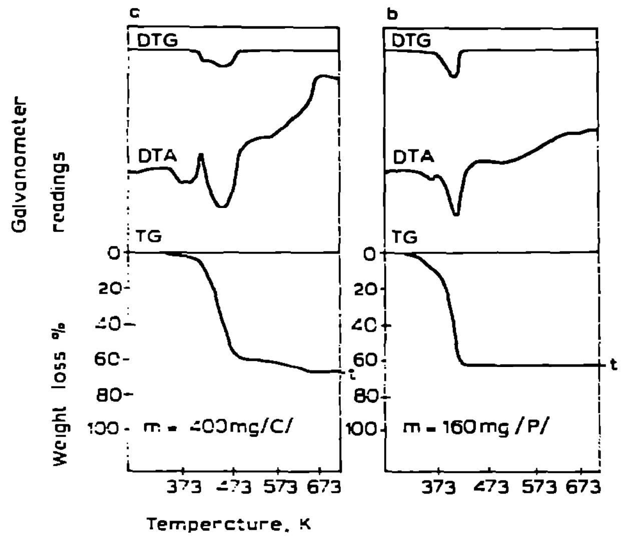

Fig. 4. Thermal analysis of $H_2PbCl_6 \cdot 4$ DMA.

removal of volatile products, the chlorine removed in the stream of inert gas was close to the stoichiometric quantity. The corresponding thermal processes recorded under these conditions by thermal analysis are very simple (see Figs. 1c, 2b, 3c, 4b). Such factors as large sample mass, slower flow rate of inert gas and presence of a layer of inert component (Table 1), which hinder the removal of volatile products, decrease the amount of chlorine in the gas stream. Under these conditions secondary reactions are likely to occur between chlorine and the amides or their hydrochlorides. These reactions occur mainly in the condensed phase, within the crucible, since the results of thermal analyses differ markedly when carried out under different conditions.

Apart from chlorine, amides or their hydrochlorides (the latter appearing only during decomposition of the $H_2PbCl_6 \cdot 4$ DMA adduct), other compounds were detected. Some of them are produced by thermal degradation of the amides, e.g.

$$HCON(CH_3)_2 \rightarrow CO + (CH_3)_2NH \qquad (3)$$

$$RCON(CH_3)_2 \rightarrow RCN + ... \qquad (4)$$

The products of these reactions have usually been detected during pyrolysis of amides [21—25].

The thermal degradation of amides can be markedly accelerated in the presence of acids, e.g. HCl [25], whose catalytic activity has been explained in terms of formation of polar species. Similar species occur in the systems studied, since both $PbCl_4$ and H_2PbCl_6 are strong Lewis acids. Hence a contribution to the thermolysis from intramolecular processes can be expected [11], e.g.

$$PbCl_4 \cdot 2\,DMF(s) \rightarrow PbCl_2(s) + DMF(l) + COCl_2(g) + (CH_3)_2NH(g) \qquad (5)$$

If this contribution was significant, however, the results of thermal analyses would be independent of sample weight.

Chlorine, liberated during thermal decomposition, is both a strong oxidant and an electron acceptor [26]. Hence, the contribution to the chlorination reactions should be significant. This was confirmed by our results. Secondary chlorination reactions can be written as follows

$$CO(g) + Cl_2(g) \rightarrow COCl_2(g) \qquad [27] \tag{6}$$

$$RCON(CH_3)_2 + Cl_2 \rightarrow HCl + ... \tag{7}$$

and

$$(CH_3)_2NH(g) + HCl(g) \rightarrow (CH_3)_2NH \cdot HCl(s) \tag{8}$$

because this hydrochloride was previously detected among the thermolysis products of $PbCl_4 \cdot 2$ DMF [11].

The DMF and DMA complexes of $PbCl_4$ and H_2PbCl_6 are less stable than the previously studied complexes of these compounds with aromatic bases [12]. This can be explained in terms of the weaker electron-donating properties of these amides. The complex course of the thermolysis of both groups of compounds is due to the presence of chlorine in the reactants; this is liberated during reduction of Pb(IV) to Pb(II), which occurs readily [27]. Chlorine is responsible for a different course of thermolysis of this group of compounds compared with thermolysis of other complexes of amides.

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