

Thermal Decomposition Studies of Some Organo-lead Compounds

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The thermal decompositions of tetraphenyl-lead, hexaphenyl-dilead, triphenyl-lead chloride and triphenyl-lead hydroxide have been studied in a controlled furnace of an automatic recording thermobalance. Some probable decomposition mechanisms have been suggested.

A SURVEY of the literature^{1,4} reveals the organo-element compounds of the fourth main group are thermally more stable than organo-lead compounds. Most of the organo-lead derivatives decompose on heating to temperatures between 100°-200°C. These compounds are hydrolytically stable and are not affected by atmospheric oxygen. Phenyl-lead derivatives have been reported to be more stable than the alkyl-lead derivatives. The decomposition studies have been made in solutions using a series of solvents, but no attempt has been made to study the effect of gradual heating on solid samples.

In view of the above facts, it was considered worthwhile to study the effect of heat on some phenyl-lead derivatives. Four compounds i.e. tetraphenyl-lead, hexaphenyl-dilead, triphenyl-lead chloride and triphenyl-lead hydroxide were chosen and were heated under reduced pressure as well as inside a specially designed furnace of an automatic recording thermobalance.

Experimental

The samples were heated inside the furnace of a mass flow type thermobalance (Stanton) at a rate of 4°C/min. The loss in weight and rise in temperature was automatically recorded. Some of the volatile fragments were trapped and analysed.

The change in weight of the samples with the rise in temperature has been shown in Fig. 1. The loss in weight per minute was calculated⁹ from the original graph and plotted against temperature in Fig. 2. The differential thermal graphs (D.T.G.) obtained from the plot shows the rate of decomposition and formation of unstable intermediate compounds.

For estimation of carbon and hydrogen standard methods of analysis have been used¹⁰. Anhydronc was used for absorption of water and ascarite for absorption of carbon dioxide. The percentage error in C and H determination was 0.5% and 3% respectively.

A few mg of the sample was dissolved in nitric acid and lead analyzed colorimetrically by dithizone method¹².

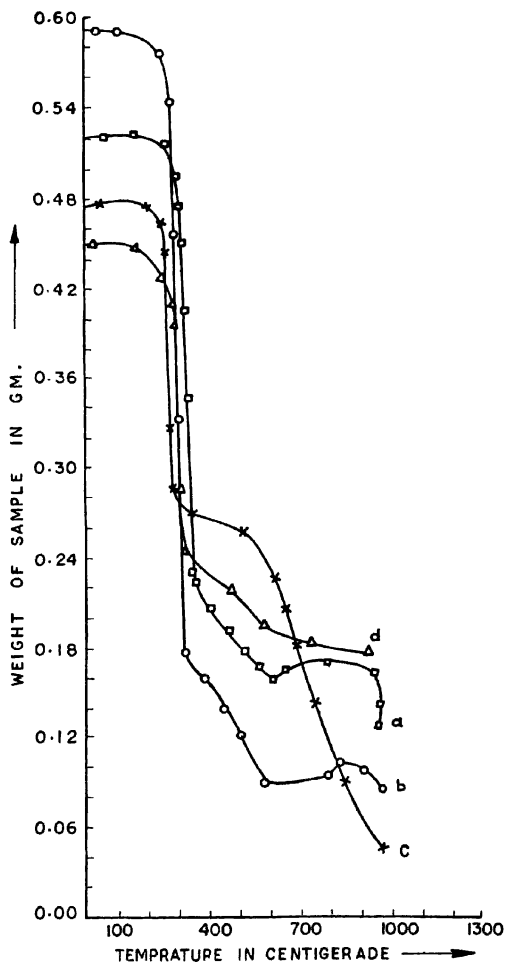


Fig. 1

The result of these analyses are given in the Table 1.

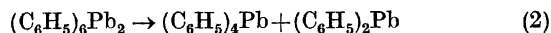
Results and Discussion

The above mentioned derivatives on heating under reduced pressure give tetraphenyl-lead in quantitative yield, which sublimed above 240°C.

TABLE 1. 1 G OF EACH COMPOUND WAS TAKEN IN EACH CASE

Compound	Temp., °C & 2 mm	Wt. of sublimed product	Analysis of sublimed product					
			Found %			Calculated %		
			C	H	Pb	C	H	Pb
PbPh ₄	285	0.9187	59.0	2.36	38.63	55.9	3.88	40.22
Ph ₆ Pb ₂	250—280	0.7984	58.0	2.62	39.2	55.9	3.88	40.22
Ph ₃ PbCl	220—270	0.6234	57.1	3.6	38.9	55.9	3.88	40.22
Ph ₃ PbOH	200—265	0.6936	60.7	3.2	35.1	55.9	3.88	40.22

When tetraphenyl-lead (0.524 g) was heated inside the furnace of the thermobalance, it sublimed out between 250–350°C, yield being about 57%. The remaining tetraphenyl-lead might have decomposed with the formation of free radicals and metallic lead as reported earlier². The rate of sublimation was very fast at about 300°C and became slow after 350°C. The loss in weight continued upto 580°C,



Both the decomposition processes have been reported earlier^{1,6}. If diphenyl lead is formed as shown in step 2, it is unstable and decomposes further as

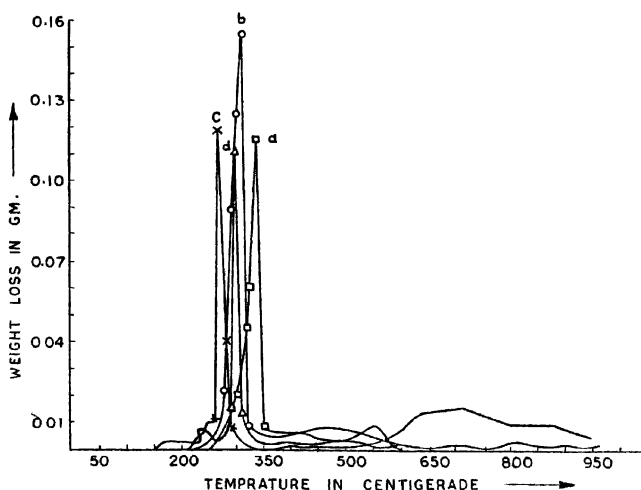
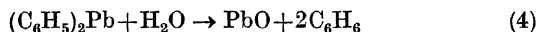
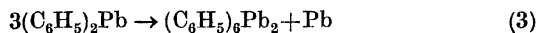
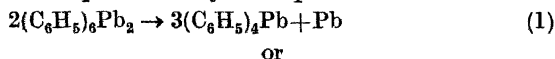


Fig. 2

but no loss was observed between 580° and 620°C. The product showed a gain in weight from 620° to 800°C. It might be due to the oxidation of metallic lead to lead oxide or due to partial conversion of lower oxide to higher oxide. In this case the colour was dark yellow which might be due to the formation of orthosilicate glass (Pb₂SiO₄) whose formation takes place above 717°C.

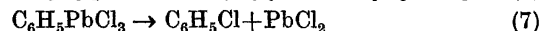
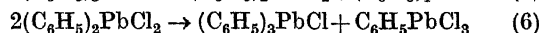
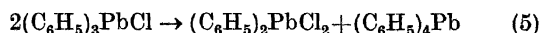
On heating above 800°C, the results showed a continuous slow loss in weight, probably due to the formation of some mixed oxides of lead. The composition of the residue could not be ascertained at any stage above 350°C. The slow loss in weight continued even on heating the sample at 950°C for an hour. The probable decomposition fragments except tetraphenyl-lead could not be ascertained due to unsuitable trapping device.

Decomposition may be represented as :



The decomposition process mentioned in step (4) has not been observed by us because no loss in weight was observed nor any benzene detected below 240°C.

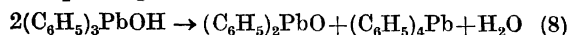
Triphenyl-lead chloride (0.477 g) did not show any loss on heating upto 230°C and after that a rapid loss between 240–300°C (Figs. 1C and 2C) was observed. Decomposition may take place according to the following scheme^{7,8}.



During decomposition a part of tetraphenyl-lead sublimed and the remaining part decomposed as described earlier; the yield of PbCl₂ was quantitative. The PbCl₂ was found to be stable upto 570°C and after that a slow loss in weight was observed which might be due to slow evaporation of PbCl₂, which

is not completed even upto 950°C. The second part of the experiment was verified by taking same weight of PbCl₂ and repeating the experiment under similar conditions.

Lastly triphenyl-lead hydroxide was heated (0.450 g). This showed a loss in weight between 150°-190°C corresponding to loss of one molecule of water.



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