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THERMAL DECOMPOSITION OF BASIC LEAD CARBONATE

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ABSTRACT

TG and DTA curves of the thermal decomposition of basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, are presented and compared with the thermogram of normal lead carbonate $PbCO_3$. The appearance of different intermediate compounds at identical experimental conditions is ascribed to the degree of perfection of the carbonate crystals. Poorly developed basic lead carbonate crystals, formed in the presence of polyglutamic acid, give no recognizable intermediate compounds.

INTRODUCTION

Numerous procedures for the preparation of lead dihydroxycarbonate, $2PbCO_3 \cdot Pb(OH)_2$, and analyses of basic lead carbonates were summarized by Mellor[1]. In this study pure $2PbCO_3 \cdot Pb(OH)_2$ was obtained by fast mixing of $2.52 \cdot 10^{-3}$ M solutions of $PbCl_2$ and Na_2CO_3 in triple distilled water, whereas the precipitation was presumably started by homogeneous nucleation[2]. The structure of the precipitate was determined by X-ray diffraction. To the best of our knowledge the thermal decomposition of $2PbCO_3 \cdot Pb(OH)_2$ has not been worked out. As the lead hydroxide and lead carbonate decompose at close regions of temperature, it was interesting to determine whether the decomposition steps of the hydroxide and the carbonate components in the complex basic carbonate were distinctively separable.

Duval[3], reporting decomposition studies of the normal carbonate, $PbCO_3$, concludes that an intermediate basic carbonate $PbCO_3 \cdot PbO$ is formed when about one half of the carbon dioxide has been given off. Garn and Kessler[4] investigated the decomposition of normal lead carbonate heated in air, using regular uncovered crucibles and crucibles with the top on, in order to avoid oxidation of the obtained PbO. They attributed the weight losses to the sequence $PbCO_3 \rightarrow PbO \cdot PbCO_3 \rightarrow 2PbO \cdot PbCO_3 \rightarrow PbO$, which could be computed on the basis of distinguishable weight-loss steps in the ratio 3:1:2. Actually the presented thermogram shows steps at a ratio 2:1:2, which would indicate more complex intermediate oxycarbonates as for instance $2PbO \cdot 3PbCO_3$[1]. The beginning of decomposition, as reported, is at about 210°C in the open sample and at about 300°C in the covered one.

Solid lead hydroxide, with the simple formula $Pb(OH)_2$, has not yet been successfully prepared. A truly hydroxylated product $Pb_3O_2(OH)_2$ decomposes from 175°C on[5]. No data about completion of PbO formation are available.

In this study, the thermogram of the basic lead carbonate $2PbCO_3 \cdot Pb(OH)_2$, which includes simultaneous TG and DTA curves, is compared with the thermogram of $PbCO_3$ obtained at identical experimental conditions. The effect of crystal perfection of the substance to be decomposed on the existence of distinct intermediate stages is also investigated and discussed.

EXPERIMENTAL

Simultaneous TG and DTA determinations were carried out on a Mettler thermoanalyzer under controlled flow of purified argon at $5\ l\ h^{-1}$.

The weights of the samples ranged from 24.01 mg to 34.84 mg. The heating rate was $4°C\ min^{-1}$. The "expanded weight" sensitivity for TG measurements was 1 mg per recorder span but for clarity only the ten-fold condensed weight loss signal was depicted on the diagrams. The DTA sensitivity was $50\ \mu V$ per recorder span.

The filtered powders of lead carbonates were washed with acetone and dried in partial vacuum at 80°C for a period of 2 h.

RESULTS AND DISCUSSION

The decomposition of $PbCO_3$, as evidenced by the TG curve (Fig. 1), under the experimental conditions employed in this study, follows a simple pattern of two unequal weight-loss steps. The weight of the sample was 34.84 mg; the theoretical weight loss on the evolution of one molecule of CO_2 is 1.91 mg. The measured values of the weight loss steps are 3.82 and 1.92 mg. The intermediate compound can be easily and precisely identified as $PbCO_3 \cdot 2PbO$. The decomposition starts at 220°C and is finished at 380°C.

The DTA curve also shows the beginning of decomposition at 220°C. The two endothermic peaks accompany the two decomposition steps and the ratio of their areas fit well with the 2:1 sequence. The first peak is asymmetric and its minimum appears in the temperature where the second CO_2 molecule, out of the three, is evolved.

The thermogram of $2PbCO_3 \cdot Pb(OH)_2$ is presented in Fig. 2. The sample weight was 28.1 mg and the weight loss calculated on the basis of this formula is 3.84 mg. The measured weight loss was 3.85 mg, confirming the conclusions of X-ray analysis that the precipitate is well crystallized, homogeneous and is exactly described by its formula. The theoretical weight loss corresponding to the decomposition step $2PbCO_3 \cdot Pb(OH)_2 \rightarrow 2PbCO_3 \cdot PbO + H_2O$, is 0.65 mg. The decomposition of the basic carbonate begins at 140°C and it seems eminently probable that the first weight-loss step is due to the evolution of the H_2O molecule. On reaching the temperature of 225°C, which is the temperature at which CO_2 evolution begins, the measured weight

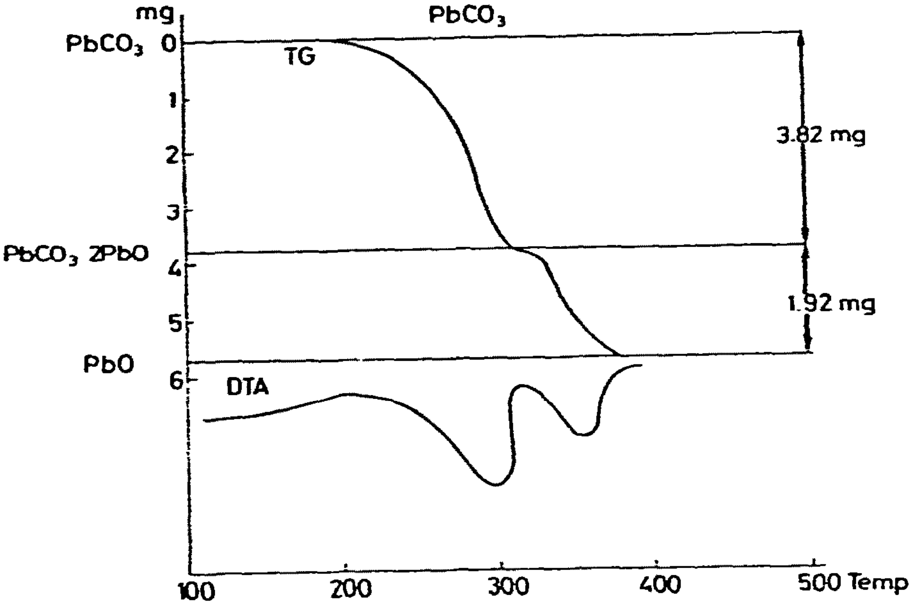

Fig. 1. Thermogram of normal lead carbonate. Sample weight, 34.84 mg.

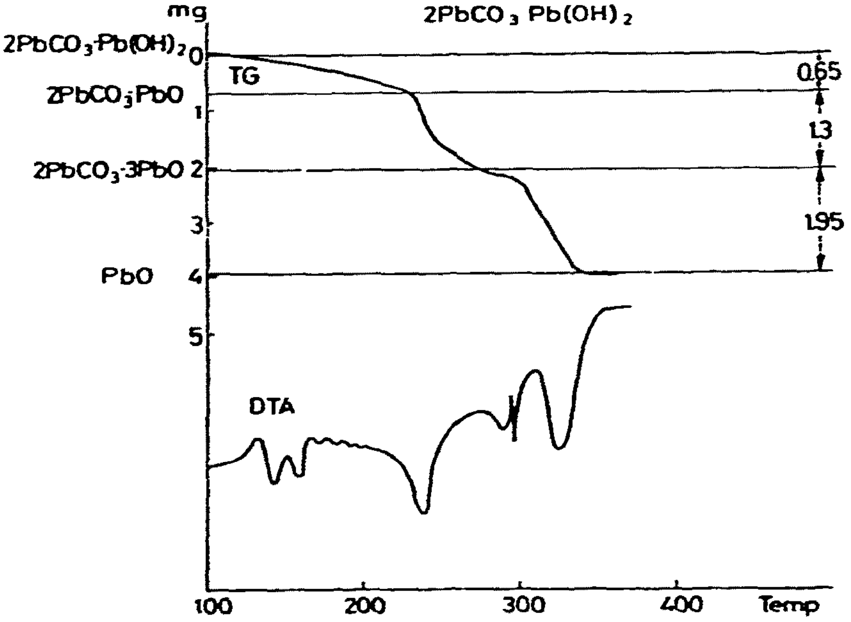

Fig. 2. Thermogram of basic lead carbonate. Sample weight, 28.10 mg.

loss was 0.65 mg, and was followed by a significant change of the slope. The overall weight loss from 225 to 360°C is 3.2 mg, in excellent agreement with the calculated loss of 3.19 mg associated with the decomposition $2PbCO_3 \cdot PbO \rightarrow 3PbO + 2CO_2$. This weight loss is subdivided differently from the sequence of pure $PbCO_3$ decomposition steps, although all the experimental conditions in both cases were identical.

The steps of $PbCO_3$ decomposition reported by Duval[3] and by Garn and Kessel[4] differ between themselves and each is different from those presented in this study. Usually such minor discrepancies are thought to result from a whole set of factors including different equipment, geometry, weight of sample, atmosphere, rate and mode of heating, restriction of decomposition products, etc. In the present case the experiments were carried out under identical conditions but for the $2PbCO_3 \cdot PbO$ the ratio of the weight-loss steps 1.35 mg:1.95 mg, i.e., a ratio of 2:3, indicates that the sequence is:

$$2PbCO_3 \cdot Pb(OH)_2 \xrightarrow{-H_2O} 2PbCO_3 \cdot PbO \xrightarrow{-2CO_2} 2PbCO_3 \cdot 3PbO \xrightarrow{-3CO_2} PbO$$

The only conceivable difference between the decomposition process of $PbCO_3$ and that of the basic carbonate is that on reaching the point of 220°C, the normal carbonate is in the form of whole crystals whereas the basic carbonate has an already partly ruptured structure following the H_2O evolution. It seems that crystal perfection significantly affects the decomposition sequence.

The DTA analysis confirms the conclusion drawn from TG. The first step of H_2O is accompanied by an endothermic split-up peak. The fact that two or even more DTA peaks may correspond to a single mass-loss step was shown particularly in cases of deaquation[6].

The evolution of two CO_2 is accompanied by a single symmetric endothermic peak with its minimum at 240°C. The transition $2PbCO_3 \cdot PbO \rightarrow 2PbCO_3 \cdot 3PbO$ is accompanied by a small sharp exothermic peak. It is interesting to note that the experimental TG curve presented by Garn and Kessler[4] indicates that $2PbCO_3 \cdot 3PbO$ is one of their intermediates. Actually their 2:1:2 weight loss sequence indicates:

$$5PbCO_3 \xrightarrow{-2CO_2} 3PbCO_3 \cdot 2PbO \xrightarrow{-CO_2} 2PbCO_3 \cdot 3PbO \xrightarrow{-2CO_2} 5PbO$$

According to their diagram (Fig. 4, ref. 4) the demarcation associated with the appearance of $2PbCO_3 \cdot 3PbO$ is remarkably sharp.

The final decomposition is associated by the endothermic peak at 320°C. The ratio of the DTA peaks of CO_2 evolution indicates that more CO_2 evolves in the second step than in the first one.

Although there is no doubt that different experimental conditions may result in different decomposition courses, the above presented comparison between the decomposition steps of normal and basic lead carbonates, strongly indicates that the degree of crystal perfection can appreciably affect the course of a decomposition reaction, giving different intermediate compounds.

This point may be strengthened by comparing the presented thermograms with a thermogram of extremely poorly developed crystals of $2PbCO_3 \cdot Pb(OH)_2$ (Fig. 3). As already mentioned the structure of the basic carbonate was determined by X-ray diffraction. The X-ray analysis of the crystals precipitated by fast mixing of $PbCl_2$ and Na_2CO_3 gives sharp, well-developed peaks. Their values are in excellent agreement with the ASTM standard. However, when the precipitation is carried out in the presence of several ppm of polyglutamic acid (PGA), the crystals are very badly developed. These crystals, when subjected to X-ray analysis, give in some cases appreciably broadened peaks and in some cases the recognizable pattern is almost lost, leaving only few barely distinguishable smeared out peaks[2]. The difference between the well-developed crystals precipitated from the pure solution and the almost amorphous basic lead carbonate formed in the presence of PGA traces is also evidenced by SEM photomicrographs[2].

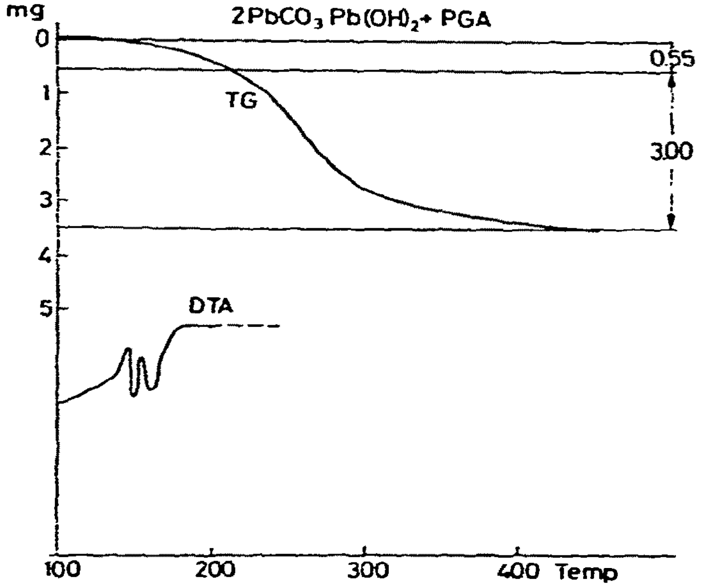

Fig. 3. Thermogram of basic lead carbonate precipitated in the presence of 10 ppm polyglutamic acid. Sample weight, 24.01 mg.

The thermogram in Fig. 3 shows the decomposition of such poorly developed crystals. The sample weight in this case was 24.01 mg and the total weight-loss should have been 3.25 mg. The actual loss was 3.55 mg. In the two previous cases, the difference between the calculated and experimental values did not exceed 0.01 mg. The 0.3 mg difference is not an operational error, as was confirmed by repeated analyses, but stems presumably from the coprecipitation of PGA with the precipitating crystals. The percent of PGA in the crystals is 1% according to the data. An admixture of 1–2% is rarely sufficient to destroy the X-ray pattern of the host crystals, but it seems that in this case the effect of PGA on basic lead carbonate is very significant. The decomposition reaction of basic lead carbonate with PGA terminates at 430°C, whereas, when the crystal did not contain any admixture, it was finished at 350–370°C. Moreover, the residues in the last reaction was strongly coloured. All these support the interpretation that the organic matter was coprecipitated with the carbonate, significantly changing the crystal perfection and was decomposed between 380–430°C. The very poorly crystallized solid phase, when subjected to heating did not yield any defined intermediate compound.

The first part of the DTA curves gives the endothermic split-up peak of water evolution. The rest of the curve is erratic and non-reproducible, and is therefore not included in the thermogram, confirming previous explanations.

It may be concluded that the degree of perfection of crystals is among the important factors which affect the course of thermal decomposition and the nature of the intermediate compounds.

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