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Note

A NOTE ON THE THERMAL DECOMPOSITION OF LEAD THIOSULPHATE

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There have been few studies of the thermal decomposition of metal thiosulphates. These compounds have found important applications in photography where the sodium and silver compounds are particularly useful. The thiosulphate that has been most studied by thermoanalytical techniques is sodium thiosulphate [1,2]. It has recently been studied using TG and Raman spectroscopy and has been found to decompose giving a mixture of polysulphides. In the light of this study it was felt to be of interest to examine the thermal decomposition of a heavy metal thiosulphate such as lead(II) thiosulphate. This compound has found application in aspects of thermal printing [3]. It is very readily prepared from a mixture of a soluble lead(II) salt and a soluble thiosulphate.

EXPERIMENTAL

A solution of lead(II)ethanoate(acetate) (0.01 mol) in water (10 cm^3) was added to a solution of sodium thiosulphate (0.01 mol) in water (10 cm^3). The white precipitate which formed immediately was washed with water, ethanol and finally diethyl ether [4]. (Analysis: Pb found 64.7%; calculated 64.9%.) Lead(II) sulphide was prepared by the published method [5]. (Analysis: Pb found 84.5%; calculated 86.6%.)

Reagents were BDH AnalaR grade when available. Lead(II) sulphate was used without further purification. TG was carried out using a Stanton TR-1 thermobalance in still air or a flow of nitrogen, using a heating rate of 4°C min^{-1} and samples of mass between 0.5 and 1.0 g. Infrared spectra were recorded using the KBr disc technique in a Perkin-Elmer 137 spectrophotometer.

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RESULTS AND DISCUSSION

Preliminary work showed that on heating at temperatures above 600°C in the absence of air, lead thiosulphate decomposed to produce metallic lead.

The thermogravimetric curves in air and under nitrogen are shown in Fig. 1 and are summarised in Table 1. It is clear that these show significant

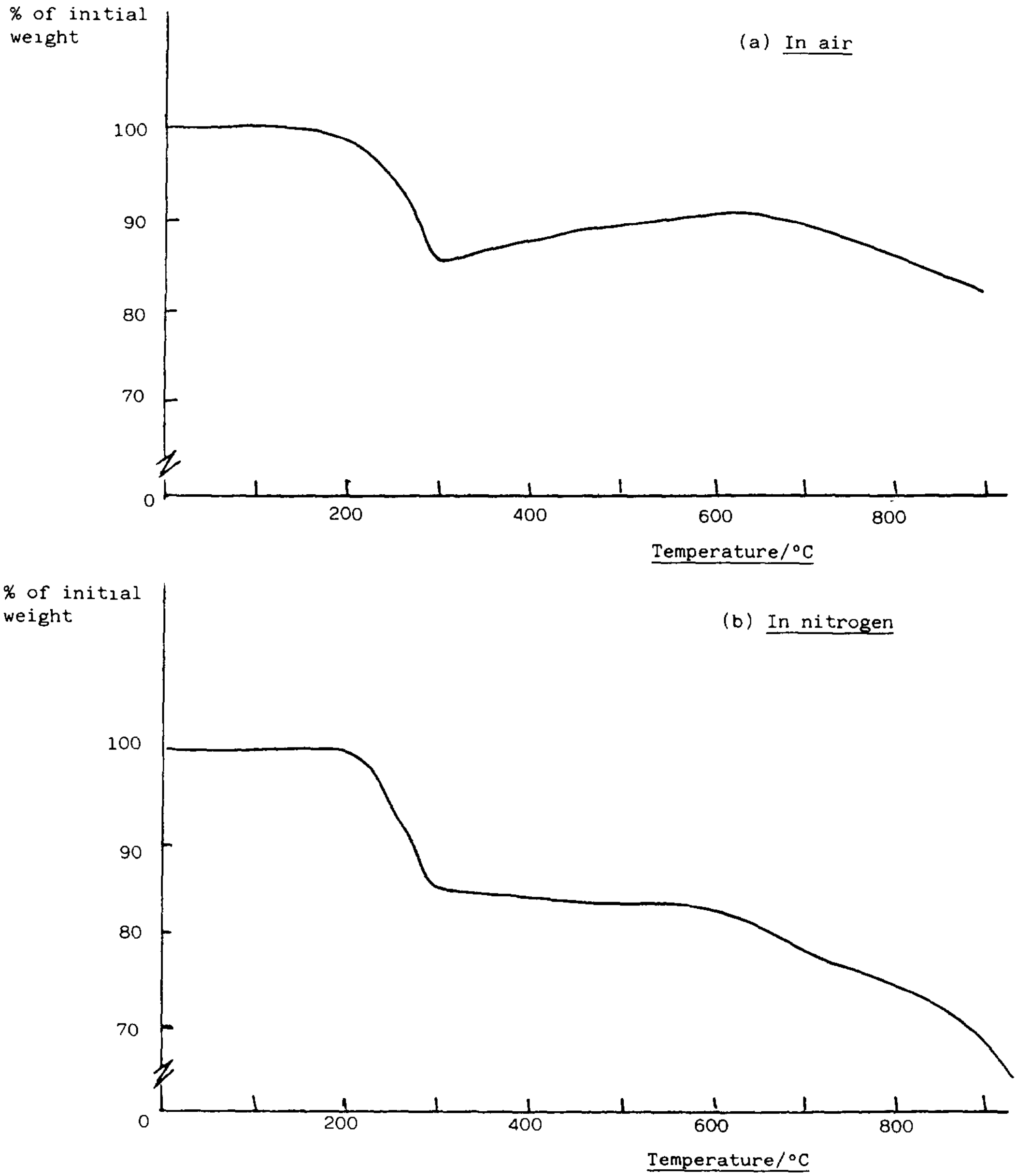

Fig. 1. TG Curves for lead(II) thiosulphate.

TABLE 1

Temp (°C)	Atmosphere	% Weight change	Proposed reaction	Theoretical % weight change (based on original compound)
200	Air	−15.2	$2PbS_2O_3 \rightarrow PbSO_4 + PbS + S + SO_2$	−15.05
260	Air	+4.8	$PbSO_4 + PbS + O_2 \rightarrow 2PbSO_4$ (incomplete because $PbSO_4$ decomposes at 650°C before all PbS has reacted).	+10.03
200	Nitrogen	−15.9	$2PbS_2O_3 \rightarrow PbSO_4 + PbS + S + SO_2$	−15.05
600–900	Nitrogen	−17.0	$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2$	−20.06

differences. In air there is an initial loss in weight followed by a gradual weight gain, starting at about 300°C and continuing until a final loss in weight occurs starting at about 680°C. At 900°C the sample consisted of a white powder.

Under nitrogen an initial weight loss, beginning at about 200°C, is followed by a plateau and finally by weight losses beginning at about 620 and 700°C respectively. Percentage weight changes are recorded in Table 1 together with suggested reactions.

Recently Mamylow, Lomowski and Boldyrew [6] studied the thermal decomposition of lead(II) thiosulphate up to 220°C. The results given here in this range are in broad agreement with those of these workers, though they worked in vacuo rather than under nitrogen. However, above 220°C in air there is a small (4.8%) weight gain similar to that which is observed when a sample of lead(II) sulphide was subjected to TG in air. The reaction is not quantitative as lead(II) sulphate itself has been shown to decompose at elevated temperatures giving yellow glassy lead(II) oxide [7]. At elevated temperatures under nitrogen the second stage of the reaction gives a weight loss at about 620°C which is attributed to the reaction between lead(II) sulphide and lead(II) sulphate to give metallic lead. (This is similar to the reactions which take place in the smelting of lead ores.) It was initially thought that this was a solid state reaction so an additional experiment was carried out in which a layer of lead(II) sulphide in a crucible was separated from a layer of lead(II) sulphate by a thin layer of aluminium oxide. After this mixture had been heated in the thermobalance, metallic lead could be seen in the product. A separate experiment using lead(II) sulphide alone showed that it began to vaporise under thermobalance conditions between 700°C and 800°C. The formation of metallic lead thus appears to be the result of a reaction between solid lead(II) sulphate and gaseous lead(II) sulphide.

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