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Note

THE EFFECT OF PURGE GAS FLOW RATE ON THERMOGRAVIMETRIC EXPERIMENTS

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This paper describes research carried out to elucidate the reasons for the unusual behaviour of lead azide, $Pb(N_3)_2$, in thermogravimetric TG and differential scanning calorimetry DSC experiments reported by other workers [1]. They noted that in a DSC experiment $Pb(N_3)_2$ behaved in the expected manner (i.e. one decomposition peak at ~ 300°C spread over a relatively narrow temperature range) but in TG runs it decomposed gradually over the temperature range 100–400°C.

EXPERIMENTAL

TG and DSC runs were carried out in a Perkin-Elmer DSC2 and a Stanton-Redcroft TG 750 using γ-$Pb(N_3)_2$ at a heating rate of 10°C min^{-1}, with Ar and N_2 as purge gases. The results obtained were similar to those previously reported. It was noted that the materials remaining at the end of these experiments (particularly the TG) were coloured in shades varying from grey/yellow to orange/red. This coloration is strongly suggestive of the formation of lead oxides, rather than pure lead which would be silvery grey.

Coloration could be due either to the formation of an oxide from impurities (such as carbonate) or from the presence of oxygen or carbon dioxide in the purge gas. In order to discover which of the two possible sources of oxygen was the more important, samples of $Pb(N_3)_2$ (~ 3 mg) were placed in tubes which were then evacuated and sealed. The tubes were placed in an oven and heated to ~ 400°C and the azide decomposed in vacuum. In all cases the resulting residue was grey, indicating that the coloration was due to purge gas impurities.

As the coloration produced in the DSC was much less marked than in the TG it seemed that the difference in behaviour could be due to the differing "atmospheric conditions" in the two pieces of equipment. The main differences between the systems are

(1) the total volume of gas in the DSC is very small and it can be quickly purged and replaced by the purge gas;

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(2) in the DSC the sample is covered and the purge gas does not flow freely around and over the sample as it does in the TG.

In order to have the atmospheric conditions in the TG similar to those in the DSC, it would be necessary to cover the sample pan and also to allow the purge gas to flow through the system at a high rate for a long time in order to clean the equipment of air. A large number of experiments were therefore carried out in the TG on samples which were in sealed pans with a ~ 0.1 mm diameter hole in the lid to allow decomposition gases to escape. The runs were carried out using a range of purge gas flow rates, with argon as the purge gas, and at a heating rate of 10°C min^{-1}. In all cases the purge gas was allowed to flow for at least half an hour before commencement of the experiment.

RESULTS

Some of the results obtained are illustrated in Fig. 1a–c. It can be seen that as the argon flow rate is increased, the result (one sharp decomposition step at ~ 300°C) becomes very similar to that obtained from the DSC (Fig. 2). In all cases the mass of residue was slightly more than that which would

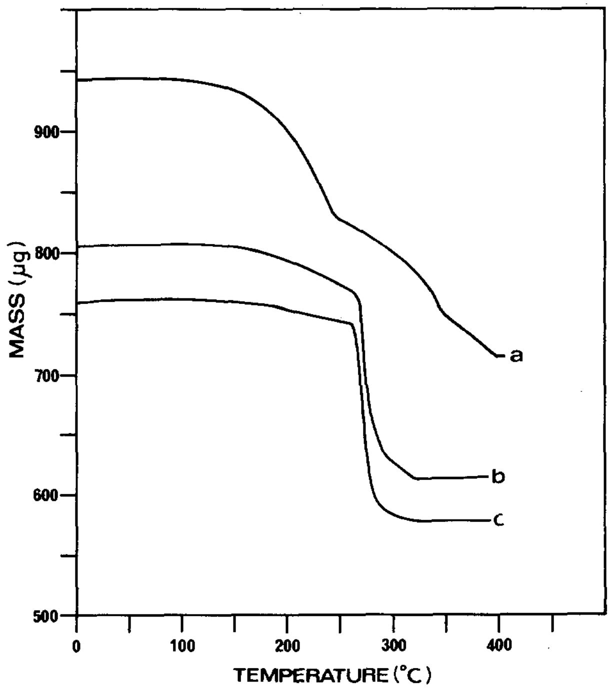

Fig. 1. TG traces from decomposition of γ-$Pb(N_3)_2$. Argon flow rate = 7 cm^3 min^{-1} (a); 60 cm^3 min^{-1} (b); and 100 cm^3 min^{-1} (c).

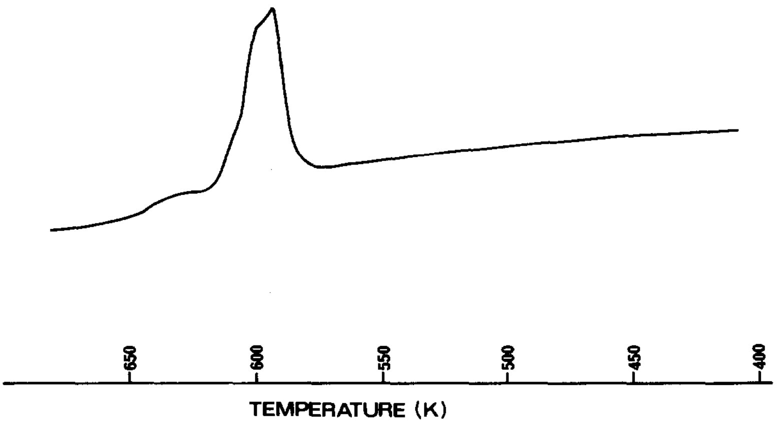

Fig. 2. DSC trace for decomposition of γ-$Pb(N_3)_2$.

be obtained if the sample had been completely reduced to lead, indicating the presence of impurities (oxides). The chemical reactions taking place are not clear but the azide is presumably being attacked by O_2 (and/or H_2O and CO_2) to yield oxide and N_2. The affinity of lead for oxygen is clear from the way freshly exposed lead surfaces quickly tarnish (in fact finely divided lead

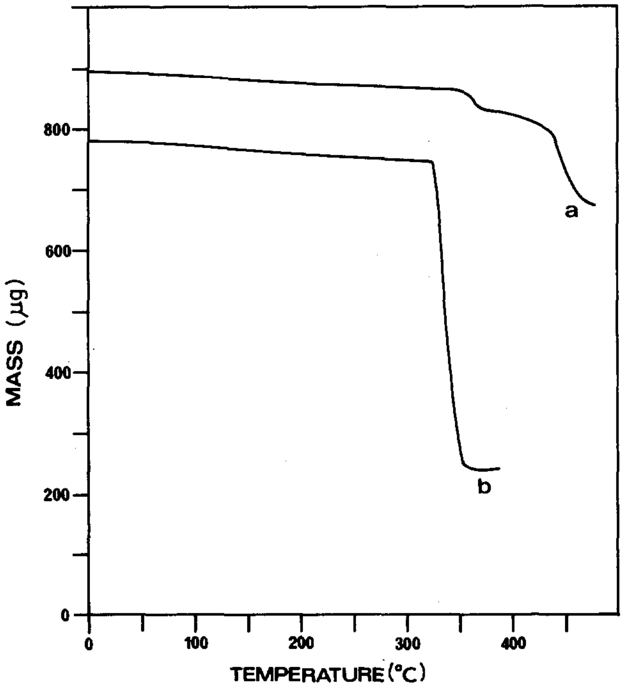

Fig. 3. TG traces for decomposition of NaN_3. (a) No purge gas flow; (b) argon flow rate 100 cm^3 min^{-1}.

is pyrophoric) whereas silver (whose azide does not produce this effect) is only slowly oxidised. The relative instability of $Pb(N_3)_2$ is also shown by the way it is rapidly converted to carbonate in the presence of high concentrations of CO_2 and water vapour [2].

One might expect this effect to be even more marked in the case of materials such as NaN_3 which contain highly reactive metals, and a TG experiment using NaN_3 did indeed show a very marked effect (Fig. 3a, b). The sample for which the system was not purged decomposed to sodium oxide and the sample for which the system had been well purged (100 cm^3 min^{-1} of Ar for 1 h before the run) decomposed to metallic sodium which showed a dramatic weight increase on exposure to air after completion of the experiment, due to the formation of oxide. The observations of Tang [3] that low gas flow rates gave anomalous results in TG experiments on lead(II) 2,4-dinitroresorimate, with the production of a red product, can also be explained by the presence of oxygen due to the low purge gas pressure in the TG.

Although the mechanisms of the reactions involved have not been elucidated it is clear from this work that extreme care should be taken during the use of metallic compounds in TG experiments, and that it is very important to ensure that the system has been fully purged of all traces of oxygen and that the internal purge gas pressure is kept sufficiently high to prevent seepage of oxygen into the system.

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