Thermochimica Acta, 105 (1986) 111–116
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

OBTENTION, THERMAL BEHAVIOUR AND STRUCTURAL STUDY OF THE DIOXYNITRATES OF LEAD

M.E. GARCIA-CLAVEL, M.J. MARTINEZ-LOPE, M.T. CASAIS-ALVAREZ and A. KILANY

U.E. de I. de Termoanálisis y Reactividad de Sólidos del C.S.I.C., Serrano 115, dpdo, 28006, Madrid (Spain)

(Received 27 January 1986)

ABSTRACT

We have studied the hydrated and anhydrous dioxynitrate of lead. $Pb(NO_3)_2 \cdot 2PbO \cdot 1.5H_2O$ is obtained by precipitation at 0°C from a 0.75 M lead nitrate solution with concentrated ammonia at a rate of 1.5 ml min^{-1}. By heating between 150 and 300°C the hydrated dioxynitrate gives $Pb(NO_3)_2 \cdot 2PbO$. The progressive calcination of this compound gives PbO with intermediate formation of $Pb(NO_3)_2 \cdot 5PbO$.

The hydrated and anhydrous lead dioxynitrate samples were studied by chemical analysis, thermogravimetry, differential thermal analysis, infrared spectroscopy and X-ray powder diffraction.

Both dioxynitrates have a laminar structure.

INTRODUCTION

In a previous paper [1], we gave the results obtained from studying the obtention and thermal behaviour of a lead monohydroxynitrate. We established the conditions necessary for the obtention (ratio of lead nitrate/ammonia, temperature, rate of addition of the reagent and rate of stirring). However, with the same ratio of lead nitrate to ammonia and the same temperature, but modifying the rate of addition of ammonia and aging of the precipitate in the mother liquors for 30 min, we obtained a sample of a different basic nitrate with the formula $Pb(NO_3)_2 \cdot 2PbO \cdot 1.5H_2O$.

Workers who have studied this compound do not agree on its formula. Byé [2] and Fauchèrre [3] give the formula as $Pb(NO_3)_2 \cdot 2Pb(OH)_2$, while other authors, such as Heubel [4] and Brusset [5] give the formula as $Pb(NO_3)_2 \cdot 2PbO \cdot xH_2O$, (Heubel reported $x = 1$ Brusset $x = 2$ or 2.5, depending on the drying conditions of the precipitate).

However, neither author employed an adequate technique for distinguishing between hydroxyl groups and water molecules. Apparently dissolution of the lead oxynitrate in a known amount of nitric acid, and back titrating the

0040-6031/86/$03.50

excess with sodium hydroxide solution, allows the ratio nitrate/oxide in the precipitate to be found, but does not allow for determination of the existence of OH^- groups, as some authors affirm.

EXPERIMENTAL

Starting materials

$Pb(NO_3)_2$, Merck, r.a.; NH_4OH, Merck, r.a.

Preparation of the samples

Samples were obtained by precipitation from a 0.75 M lead nitrate solution with concentrated ammonia at 0°C. For 60 ml of lead nitrate solution, 5 ml of ammonia were added at a rate of 1.5 ml min^{-1}. The solution was stirred slowly during the addition, and after precipitation, was continued for 30 min. The precipitate was filtered using a N.4 coarse filter, washed with ethanol, and dried in vacuo.

The composition of the precipitate was determined by quantitative chemical analysis: NO_3^-, Perkin-Elmer 240 analyzer; Pb^{2+}, complexometric titration with EDTA and indicator Eriochrome Black T.

Apparatus

TG

A Chevenard thermobalance (model 93) from Adamel was used with photographic recording. Heating rate was 300°C h^{-1}.

DTA

This apparatus was constructed in the laboratory using a vertical furnace and a temperature regulation system, both from Adamel. A differential chromel/alumel thermocouple was used. Heating rate was 300°C h^{-1}.

X-ray powder diffraction

A Siemens D-500 diffractometer was used with a graphite monochromater, K 805 generator and Cu $K\alpha_1$ radiation.

Infrared spectroscopy

A Perkin Elmer 599 B instrument was used. The samples were prepared as mulls using fluorolube as the mulling agent for the region 4000–1500 cm^{-1}, and KBr pellets for the region 1500–200 cm^{-1}.

RESULTS AND DISCUSSION

Thermal study

In Fig. 1 we give the TG and DTA curves of the hydrated dioxynitrate of lead.

The TG curve presents four well-defined steps. Between 60 and 150°C, the first step corresponds to the loss of ammonia sorbed by the precipitate, which is released abruptly and accounts for 1.6% of the sample weight; the second step corresponds to 1.5 mol of water of hydration. The existence of ammonia in the precipitate was proved by collection of the gases released during heating over a phenolphthalein solution. This retention of the ammonia by the precipitate does not occur in other oxynitrates of lead.

A plateau corresponding to $Pb(NO_3)_2 \cdot 2PbO$ is found between 150 and 300°C; decomposition takes place at 300–500°C in two stages, with the intermediate formation of $Pb(NO_3)_2 \cdot 5PbO$ as confirmed by X-ray diffraction [6]. At 500°C following decomposition, a second plateau appears corresponding to α-PbO and β-PbO.

The DTA curve presents four endothermic peaks which correspond to the four steps of the TG curve.

According to Martin et al. [7] the hydrated dioxynitrate of lead is transformed by heating into a mixture of hydrated monoxynitrate and hydrated heptoxynitrate of lead at 130°C as shown in the X-ray diffractograms of the different samples isolated. However, our results do not indicate this, since these stages are not observed in any of the curves in Fig. 1. Moreover, the calcination of $Pb(NO_3)_2 \cdot PbO$, which results from the dehy-

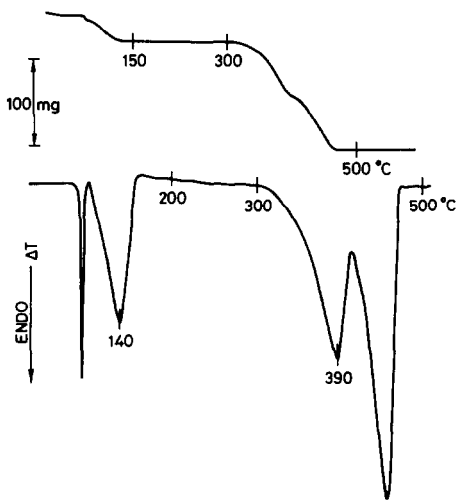

Fig. 1. TG and DTA curves. Sample weight: 1.0000 g.

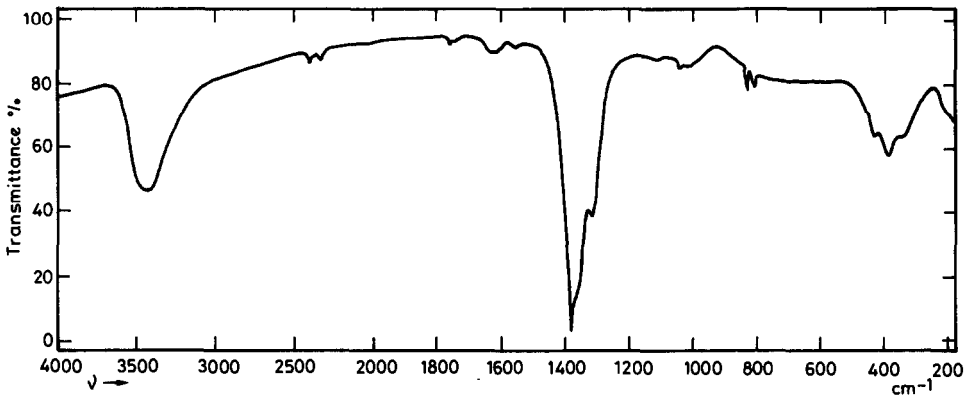

Fig. 2. IR spectrum.

droxylation of the monohydroxynitrate, leads to four different compounds (studied by us) and these are clearly visible in the TG and DTA curves of the monohydroxynitrate [1].

TABLE 1

X-ray data for $Pb(NO_3)_2 \cdot 2PbO \cdot 1.5H_2O$

d_{obs} (Å)	d_{cal} (Å)	I/I_0	$h\,k\,l$	d_{obs} (Å)	d_{cal} (Å)	I/I_0	$h\,k\,l$
7.278	7.246	24	1 1 0	2.324	2.323	4	4 2 1
6.804	6.777	54	0 0 1	2.272	2.272	6	5 1 0
5.473	5.460	25	0 1 1	2.260	2.259	13	0 0 3
4.447	4.433	3	2 0 1	2.236	2.235	10	1 3 2
4.298	4.290	34	1 2 0	2.190	2.194	4	0 1 3
4.008	3.995	12	2 1 1	2.148	2.145	4	1 4 1
3.919	3.908	7	3 0 0	2.120	2.121	5	4 3 0
3.814	3.811	12	0 2 1	2.106	2.108	7	2 0 3
3.626	3.625	4	1 2 1	2.090	2.090	6	5 2 0
3.392	3.389	45	0 0 2	2.045	2.045	6	2 4 1
3.257	3.255	13	1 0 2	2.023	2.024	8	4 3 1
3.194	3.195	100	2 2 1	1.997	1.997	3	5 2 1
3.070	3.070	27	1 1 2	1.965	1.967	3	3 3 2
2.976	2.973	22	1 3 0	1.914	1.913	6	3 1 3
2.795	2.796	9	2 1 2	1.880	1.881	6	1 4 2
2.722	2.722	30	1 3 1	1.812	1.812	4	2 4 2
2.692	2.689	4	4 0 1	1.798	1.798	5	4 3 2
2.659	2.659	23	1 2 2	1.777	1.779	11	5 2 2
2.583	2.582	6	4 1 1	1.749	1.750	6	4 4 1
2.560	2.560	18	3 0 2	1.737	1.738	9	2 3 3
2.527	2.526	5	2 3 1	1.674	1.675	5	7 0 0
2.466	2.467	13	3 1 2	1.666	1.666	7	0 1 4
2.343	2.344	3	5 0 0				

Infrared spectroscopy

The spectrum of the hydrated dioxynitrate of lead on precipitation is shown in Fig. 2. It presents the characteristic bands of water of hydration (3440 cm^{-1} (stretching), 1630 cm^{-1} (bending)), and the characteristic bands of nitrates (1380, 1360, 1320 cm^{-1} (ν_3); 810, 830 cm^{-1} (ν_2). Weak bands of nitrates are also observed at 2390 and 1740 cm^{-1}. However, the bands of the NH_4^+ group in the regions between 3300 and 3030 cm^{-1} (stretching vibration) and 1430 and 1390 cm^{-1} (bending vibration) are not visible in the spectrum. This may be due to overlapping by the vibrations of the water of hydration and nitrate.

X-ray diffraction

An X-ray diffractogram was obtained from the dioxynitrate of lead on precipitation and another from a sample taken, immediately on termination of the first endothermic peak of the DTA curve (Fig. 1), which corresponds to the loss of the ammonia retained by the precipitate. The two diffractograms are identical (Table 1). The second and third reflection of the plane

TABLE 2

X-ray data for $Pb(NO_3)_2 \cdot 2PbO$

d_{obs} (Å)	d_{cal} (Å)	I/I_0	$h\,k\,l$	d_{obs} (Å)	d_{cal} (Å)	I/I_0	$h\ k\ l$
9.441	9.425	44	1 0 0	2.407	2.409	14	1 5 3
7.121	7.136	50	1 1 1	2.351	2.352	18	0 5 3
5.933	5.939	17	1 2 1	2.307	2.307	20	2 1 4
4.839	4.830	5	1 3 1	2.230	2.225	14	4 3 2
4.686	4.712	4	2 0 0	2.187	2.186	8	2 7 2
4.253	4.242	26	2 2 1	2.160	2.159	11	−1 7 2
4.149	4.158	28	1 2 2	2.081	2.081	5	2 8 0
3.715	3.717	10	−1 0 2	2.034	2.033	9	1 7 3
3.534	3.568	9	2 2 2	1.999	1.999	4	0 7 3
3.352	3.346	12	1 5 1	1.959	1.958	11	5 0 1
3.283	3.285	20	1 4 2	1.895	1.893	10	2 9 1
3.256	3.253	15	0 4 2	1.864	1.864	6	3 5 4
3.188	3.186	60	−1 3 2	1.850	1.850	8	−4 2 2
3.140	3.142	100	3 0 0	1.822	1.822	10	−2 2 4
3.014	3.013	19	3 0 2	1.809	1.810	7	−2 9 1
2.898	2.896	76	−2 0 2	1.765	1.768	8	−1 10 1
2.836	2.822	15	2 2 3	1.713	1.713	11	−3 5 3
2.764	2.765	9	−2 2 2	1.691	1.690	5	3 4 5
2.668	2.671	19	3 4 1	1.672	1.673	5	3 7 4
2.576	2.576	11	1 6 2	1.645	1.645	13	−4 1 3
2.514	2.508	9	1 7 1	1.588	1.589	3	2 11 0
2.483	2.483	3	3 2 3	1.563	1.563	5	−2 10 0

TABLE 3

Crystallographic data

Compound	System	Parameters (Å)
$Pb(NO_3)_2 \cdot 2PbO \cdot 1.5H_2O$	Orthorhombic	$a = 11.723 \pm 0.005$ $b = 9.219 \pm 0.005$ $c = 6.777 \pm 0.004$
$Pb(NO_3)_2 \cdot 2PbO$	Monoclinic $\alpha = \gamma = 90°$ $\beta = 73°40'$	$a = 9.820 \pm 0.006$ $b = 18.561 \pm 0.01$ $c = 9.508 \pm 0.05$

001(6.804 Å) indicates that this compound is a laminar structure. In Table 2 we give the X-ray diffractogram of the anhydrous dioxynitrate of lead. In this diagram the second and third reflections also appear and therefore this compound is also of laminar structure, with a basal space of 9.441 Å.

We obtained the crystalline parameters for both compounds; these were adjusted by the least squares method, using the sub-program PARAM of the general program X-ray L-SUCRE [8], and are given in Table 3.

CONCLUSION

The following stages in the thermal transformation of the hydrated dioxynitrate of lead obtained by precipitation were established

$$Pb(NO_3)_2 \cdot 2PbO \cdot 1.5H_2O \rightarrow Pb(NO_3)_2 \cdot 2PbO \rightarrow Pb(NO_3)_2 \cdot 5PbO \rightarrow PbO$$

REFERENCES

1 M.E. Garcia-Clavel, M.J. Martinez-Lope, M.T. Casais-Alvarez and A. Kilany, Thermochim. Acta, 98 (1986) 205.
2 J. Byé, Bull. Soc. Chim. Fr., (1947) 205.
3 J. Fauchèrre, Bull. Soc. Chim. Fr., (1954) 128.
4 J. Heubel, Ann. Chim., 4 (1949) 699.
5 H. Brusset, J.J.P. Martin and Ch. Peltier, Bull. Soc. Chim. Fr., (1967) 1127.
6 M.E. Garcia-Clavel, A. Kilany and F. Burriel-Martí, in H.G. Wiedemann (Ed.), Proc. 3rd ICTA, Davos, 1971, Birkhaueser Verlag, Basel, 1972, Vol. 2, pp. 217–228.
7 J.J. Martin, C. Martin-Lefevre and E. Husson, Bull. Soc. Chim. Fr., (1973) 836.
8 Program X-ray L-Sucre, Least square unit cell refinement, Freiburg University, (1973).