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STUDY OF THE DEGRADATION IN OPEN ATMOSPHERE OF THE HYDRATED DIOXYNITRATE OF LEAD

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ABSTRACT

In this paper we have studied the evolution in open atmosphere of hydrated lead dioxynitrate. This compound reacts to humidity and CO_2 in the air and it transforms into hydrocerussite and lead monohydroxynitrate. This mixture has been studied by chemical analysis, thermogravimetry, differential thermal analysis, infrared spectroscopy and X-ray powder diffraction.

INTRODUCTION

The preparation conditions and thermal behaviour of hydrated lead dioxynitrate were given in a previous paper [1]. Reaction of this compound to both humidity and CO_2 in the atmosphere is very rapid, and it is transformed into hydrocerussite and lead monohydroxynitrate.

Although numerous authors have studied lead dioxynitrate [2–5], none of them have mentioned its instability.

EXPERIMENTAL

Samples

The sample was hydrated lead dioxynitrate, obtained according to ref. 1 and kept in a weighing bottle. Slight evolution of the sample began after 72 h. Results are presented corresponding to this hydrated dioxynitrate after 6 months.

The composition of the sample was determinated by quantitative chemical analysis: NO_3^- and CO_3^{2-}, Perkin-Elmer 240 analyser; Pb^{2+}, complexometric titration with EDTA, indicator Eriochrome Black T.

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Apparatus

TG

Chevenard thermobalance (model 93) from Adamel. Photographic recording. Heating rate: 300°C h^{-1}.

DTA

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

X-ray powder diffraction

Siemens D-500 diffractometer. Graphite monochromator. K 805 generator. Cu $K\alpha_1$ radiation.

Infrared spectroscopy

Perkin-Elmer 599B; the sample was prepared as a mull using fluorolube as mulling agent for the region 4000–1500 cm^{-1}, and KBr pellets for the region 1500–200 cm^{-1}.

RESULTS AND DISCUSSION

X-ray powder diffraction shows that the sample is a mixture of hydrocerussite and lead monohydroxynitrate; the X-ray diagram of the latter was given in a recent paper [6].

Infrared spectroscopy confirmed the X-ray powder diffraction results. Figure 1 shows the spectra of both lead dioxynitrates (a) on precipitation and (b) after six months. There are two bands in curve (b) in the region 3500–3400 cm^{-1} due to hydroxyl groups, one at 3490 cm^{-1} and the other at 3450 cm^{-1}. The bands at 2354 cm^{-1} also correspond to hydrocerussite [7], as well as the band of carbonates at 685 cm^{-1} (ν_4).

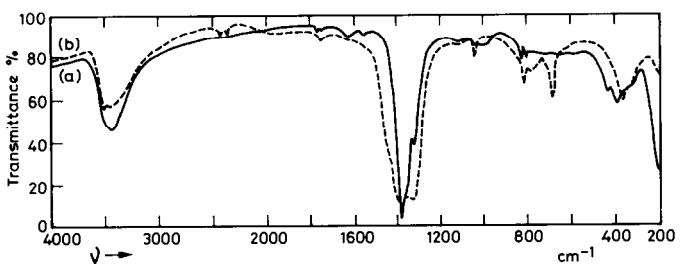

Fig. 1. IR spectra.

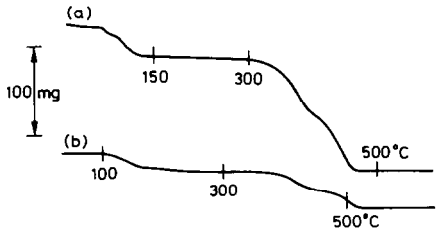

Fig. 2. TG curves. Sample weight: (a) 1.0000 g; (b) 0.3729 g.

The thermogravimetric data and the chemical analysis allow us to establish the composition of the aged samples as follows:

$$Pb(NO_3)_2 \cdot Pb(OH)_2 + 1/3[2PbCO_3 \cdot Pb(OH)_2]$$

Figure 2 shows the TG curves of the dioxynitrate on precipitation (curve a) and the aged sample (curve b). We can see from this figure that the shape of the curves is different in the initial region between 25 and 300°C.

Figure 3 shows the DTA curves of both dioxynitrates. Curve (b) confirms the qualitative results of the TG curve, and also demonstrates that the thermal behaviour of lead monohydroxynitrate is different when hydrocerussite is present; the intermediate compounds, $Pb(NO_3)_2 \cdot 1.4PbO$ and $Pb(NO_3)_2 \cdot 2.2PbO$, visible in the DTA curve of the monohydroxynitrate [6], do not appear in curve (b).

We took samples at 270 and 420°C in curve (b) (Fig. 3). The study of these samples by X-ray powder diffraction and thermogravimetry allowed us to establish the composition of both samples.

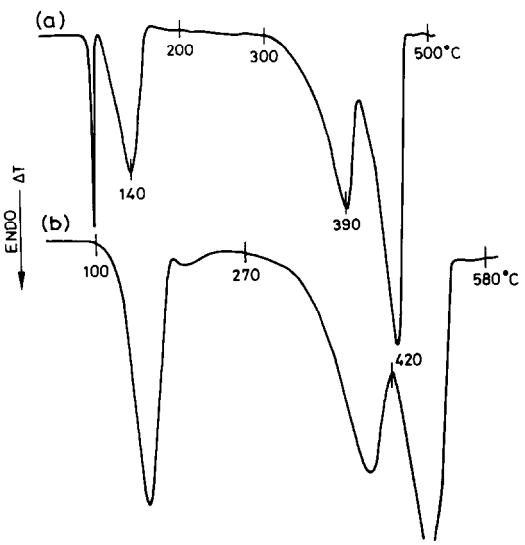

Fig. 3. DTA curves.

Sample taken at 270°C. This showed a mixture of anhydrous lead monoxynitrate (this diagram being the same as that given by Martin et al. [8] and by us [6], and lead monoxycarbonate in the proportion

$$Pb(NO_3)_2 \cdot PbO + 1/2PbCO_3PbO$$

Sample taken at 420°C. This showed a mixture of lead pentoxynitrate and lead oxide.

CONCLUSIONS

From the present study we are able to establish the following transformations of hydrated lead dioxynitrate.
(1st) At room temperature

$$Pb(NO_3)_2 \cdot 2PbO \cdot 1{,}5H_2O \xrightarrow{CO_2 + H_2O} Pb(NO_3)_2Pb(OH)_2 + 1/3\ 2PbCO_3 \cdot Pb(OH)_2$$

(2nd) By progressive heating of the aged sample

$$Pb(NO_3)_2 \cdot Pb(OH)_2 + 1/3\ 2PbCO_3 \cdot Pb(OH)_2 \xrightarrow{25-270°C}$$

$$Pb(NO_3)_2 \cdot PbO + 1/2PbCO_3 \cdot PbO \xrightarrow{270-420°C}$$

$$2/7Pb(NO_3)_2 \cdot 5PbO + 9/7PbO \xrightarrow{420-580°C} 3PbO$$

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