

**177.** *The Decomposition of Lead Nitrate in Molten Potassium Nitrate.*

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THE present work is an extension of previous work (Glass, Laybourn, and Madgin, this vol., p. 874) and concerns the nature of the decomposition products of lead nitrate in molten potassium nitrate.

Thus prepared, these products would be expected to be uniform in composition, in contrast to those formed by heating solid lead nitrate, as was done by Baekeland (*J. Amer. Chem. Soc.*, 1904, **26**, 391), who concluded that a basic salt, lead oxytetranitrate [ $\text{PbO}\cdot 2\text{Pb}(\text{NO}_3)_2$ ], was formed. This salt should contain Pb, 70.2%, but Baekeland found 68.7%, and the difference may be due to heterogeneity owing to incomplete decomposition of the nitrate. He also suggested (*loc. cit.*) that continued heating resulted in the formation of other basic nitrates.

## EXPERIMENTAL.

A mixture of 500 g. of finely ground purified salts [40%  $\text{Pb}(\text{NO}_3)_2$ , 60%  $\text{KNO}_3$ ] was heated for 24 hours at  $160^\circ$  in an electric furnace to remove moisture. The furnace was essentially a nest of tall Pyrex beakers, each wound with a length of nichrome resistance wire forming separately controlled heating circuits, and the outermost beaker was lagged with asbestos, with observation windows.

The temperature was slowly raised from  $160^\circ$  to  $357^\circ$  (compare Baekeland, *loc. cit.*), and a clear colourless melt finally obtained. Thereafter the temperature was maintained constant and, at intervals, duplicate samples of the melt (about 0.75 g.) were withdrawn, cooled, and analysed for lead by the chromate method.

After 12 hours, a sample was completely soluble in cold water and contained 40.34% of lead nitrate, estimated as lead; evidently no decomposition had occurred then. The sample at 24 hours, when extracted with ice-cold water, left an insoluble, finely divided residue, apparently white, but very pale yellow when collected on a filter. This residue, completely soluble in concentrated hydrochloric acid, contained 70.15% of lead (compare 70.2% for the oxytetranitrate). Subsequent samples gave residues which became progressively more yellow; these will be referred to as the substance A in what follows.

TABLE I.

Time, days.	% Pb in A.	% Pb in B.	$\frac{\text{Amount of C}}{\text{Amount of A}}$
$\frac{1}{2}$	No A formed.	—	—
1	70.15	70.15	—
2	70.48	—	Trace of C
3	70.68	70.60	„
6	71.20	—	„
10	71.72	71.51	0.0201
21	73.31	—	0.0421
24	73.60	72.58	0.0493
27	73.71	—	0.0531

The yellow colour of the original melt also gradually increased in intensity, but this was considered to be due largely to dissolved

nitrogen peroxide, since samples withdrawn into glass tubes extruded large quantities of this gas on solidifying.

When solid A was treated with dilute acetic acid, a large part (B) dissolved, but there remained a dark brown solid (C), which was shown, by analyses for lead and available oxygen, to be lead dioxide. The total amount of this was always very small, and its finely divided state rendered filtration very difficult. The results are summarised in Table I.

Some indication of the rate of formation of A is given by the following table, which shows the percentage of A in a given weight of melt sample :

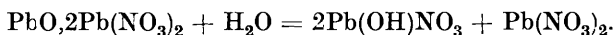
Time (days) .....	3	4	6	10	13
% A .....	0.086	0.519	1.177	2.029	2.032

After 8 days, however, a white precipitate began to separate, and this slowly accumulated. Subsequent analysis showed it to be the same as A, and the solubility of A is apparently small.

The slowness of the decomposition of lead nitrate may be due to the reversal caused by the large amount of nitrogen peroxide dissolved in the melt (compare Baekeland, *loc. cit.*).

No potassium was found in any sample of A, and aqueous extracts, which contained all of the free excess lead nitrate and potassium nitrate, were free from nitrite.

*Hydrolysis of Products.*—The first sample, entirely soluble in dilute acids, was boiled with water under reflux for 2 hours, a clear solution being obtained. On cooling, a white crystalline solid separated [Found: Pb, 72.34. Calc. for  $\text{Pb}(\text{OH})(\text{NO}_3)$ : Pb, 72.38%] and it gave reactions in solution for both a nitrate and a hydroxide. This lead hydroxynitrate was probably formed as follows :



The product A, derived from later samples of the melt, left a dark brown insoluble residue on hydrolysis, but the aqueous solution contained lead hydroxynitrate as in the first sample. This brown solid proved to be lead dioxide, identical with the substance C. The amount of C from a given weight of A was the same whether obtained by acid treatment or by hydrolysis.

Lead hydroxynitrate was known to react with carbon dioxide (Chevreul, *Ann. Chim. Phys.*, 1812, **83**, 70). This was confirmed, and the preceding hydrolyses were therefore done in a carbon dioxide-free atmosphere. Lead oxytetrannitrate itself combines with carbon dioxide to some extent, owing either to slow hydrolysis in cold water or to direct combination. The carbonate formed from it

in solution contained Pb, 79.95, 80.06% [Calc. for  $\text{Pb}(\text{OH})_2, 2\text{PbCO}_3$ : Pb, 80.13%].

*Synthetic Experiments.*—A. *Synthesis of lead oxytetranitrate.* 75 G. of a mixture of lead nitrate (40%) and potassium nitrate (60%) were fused at  $300^\circ$ , and 5 g. of litharge stirred in gradually. The first portions dissolved readily, but the later additions (dark orange at this temperature) remained for some time. Meanwhile, a light yellow solid began to deposit (compare decomposition melt after 8 days), and, as the remaining lead oxide slowly disappeared, this accumulated. Evidently the solubility limit of the product had been reached.

The melt was cooled and extracted with water, leaving a pale yellow powder, apparently the oxytetranitrate (Found: Pb, 70.38%). If higher temperatures are used, greater proportions of litharge can be dissolved, but if the temperature is allowed to fall, oxynitrates separate. However, these contain more than 70.2% of lead, indicating that secondary reactions have set in. This is similar to the progressive increase of lead content in A (see Table I).

B. *Synthesis of  $\text{Pb}_3\text{O}_4, 3\text{Pb}(\text{NO}_3)_2$ .* Red lead (2 g.) was stirred into a melt containing 20 g. of lead nitrate with 30 g. of potassium nitrate at  $300^\circ$  until the dark violet-coloured oxide completely disappeared; a clear lemon-yellow solution remained. The slow rate of dissolution ( $\frac{1}{2}$  hour) suggests that a chemical reaction is occurring. After being cooled, the yellow water-insoluble residue (resembling lead oxytetranitrate) was extracted in the usual way, and contained Pb, 73.97% [ $\text{Pb}_3\text{O}_4, 3\text{Pb}(\text{NO}_3)_2$  requires Pb, 74.02%]. This compound yields lead dioxide on hydrolysis or on treatment with dilute acids.

Similar synthetic experiments can be done in molten sodium nitrate containing lead nitrate.

#### *Discussion.*

The foregoing experiments appear to show quite definitely that the primary product in the decomposition of lead nitrate in potassium nitrate solution is lead oxytetranitrate, and presumably lead oxide is formed as an intermediate. The presence of dioxide in samples of A requires explanation. During the decomposition experiments, when a melt was heated for one month, isolated portions of it adhered to the walls of the beaker, and in these places black patches developed, which turned red when finally cooled and proved to be red lead. Doubtless, local overheating had occurred to some extent, but it seems probable that oxygen, both atmospheric and that produced in the melt, would oxidise lead oxide in the melt, and the resultant red lead combines with lead nitrate

to form a complex which appears to be  $\text{Pb}_3\text{O}_4, 3\text{Pb}(\text{NO}_3)_2$ . This again presumably forms some loose complex with lead oxytetra-nitrate, giving an apparently uniform material and not a heterogeneous mixture. Samples of A appeared homogeneous under the microscope.

The following are the reasons for assuming the formation of  $\text{Pb}_3\text{O}_4, 3\text{Pb}(\text{NO}_3)_2$ : (a) This compound has apparently been synthesised from red lead and a molten mixture of lead nitrate and potassium nitrate. (b) When the product A is treated with dilute acids, the substance containing red lead might be expected to split off lead dioxide and leave  $2\text{PbO}, 3\text{Pb}(\text{NO}_3)_2$ :  $\text{Pb}_3\text{O}_4, 3\text{Pb}(\text{NO}_3)_2 = \text{PbO}_2 + 2\text{PbO}, 3\text{Pb}(\text{NO}_3)_2$  (calc. : Pb, 72.74%), only the latter being soluble in the acid. This explanation agrees with Table I, and shows that the percentage of lead in A should increase towards a maximum of 74.02%, while that in B should approach 72.74%. (c) The behaviour of a sample of A on hydrolysis is such as would be expected for a substance containing the complex  $\text{Pb}_3\text{O}_4, 3\text{Pb}(\text{NO}_3)_2$ .

#### *Summary.*

(1) The decomposition of lead nitrate in molten potassium nitrate (maintained at 357° for 28 days) has been examined by withdrawing samples at intervals and analysing the portions insoluble in cold water for lead.

(2) It is concluded that  $\text{PbO}, 2\text{Pb}(\text{NO}_3)_2$  (lead oxytetranitrate) is slowly formed, and subsequently another oxynitrate,



is produced.

(3) Both substances are soluble in dilute acids, the latter leaving a residue of lead dioxide, and both are hydrolysed in boiling water, forming lead hydroxynitrate.

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