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MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC: THE REACTIONS OF SOME LEAD COMPOUNDS

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ABSTRACT

Lead(II) cations were soluble and considerably stabilised by nitrate melt anions but little additional stability was conferred by the presence of dissolved halide, sulphate or phosphate anions. Compounds of lead(II), except for the oxide, reacted at less than 500°C to give red lead (Pb_3O_4) as the initial product, as did lead(IV) oxide, though on long heating at 500°C lead(II) oxide was the stable product, probably because of reduction by nitrite produced by thermal decomposition of nitrate.

INTRODUCTION

For many years lead(II) appeared to be a stable cation in molten nitrate solution because many chromatographic [1,2], cryoscopic [3,4], polarographic [5–8], potentiometric [9,10], titrimetric [11,12] and electromigration [13] studies have been reported as well as the classical measurements of the solubility of lead(II) chromate in the presence of halides which gave the first values for formation constants of metal–halide complexes in molten nitrate solutions [14].

However, recently Salaha et al. [15] have reported a number of reactions involving the oxidation of lead(II) in molten nitrates ($LiNO_3$, $NaNO_3$, KNO_3, $LiNO_3/KNO_3$, $NaNO_3/KNO_3$) at higher temperatures, which parallel some hitherto unpublished studies [16] which had been undertaken as an extension of a paper on the reaction of various lead compounds with the molten nitrite eutectic [17]. The Southampton studies now reported here, which used a molten binary eutectic ($LiNO_3/KNO_3$), extend and in some cases indicate different reactions to those of Salaha et al. [15].

EXPERIMENTAL

Materials

The lithium nitrate–potassium nitrate eutectic was prepared as previously reported [18]. The lead and alkali metal compounds (AnalaR in case of

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$Pb(NO_3)_2$, PbO_2, KCl, KBr and K_2SO_4, the rest being reagent grade) were dried for 2 h at 120°C.

Measurements

Thermogravimetry was carried out on a Stanton TR-1 thermobalance as previously reported [18], the weight losses being reported as a percentage of the initial solute weight. Losses under isothermal conditions are indicated on the figures by hatched lines, the abscissae then being $100°C \equiv 50$ min.

X-ray powder diffraction was carried out using a Philips (Eindhoven) diffractometer and nickel-filtered copper K_α radiation. The d spacings and intensities were matched with those of known compounds from the JCPDS Index.

RESULTS AND DISCUSSION

Lead(II) sulphate is very soluble in the molten lithium nitrate–potassium nitrate eutectic, in fact more so than potassium sulphate (> 0.15 m and 0.07 m, respectively, at 300°C) which is unexpected in view of the usual parallelism between aqueous solubilities and those in this molten nitrate. Such solutions remained colourless until 450°C when they became yellow, darkening with increasing temperature until a brown precipitate was formed at 490°C. On cooling to room temperature this precipitate became orange in colour and after extraction with water was shown by X-ray powder diffraction to be triplumbic tetroxide (Pb_3O_4, which will be subsequently referred to by the common though non-systematic name of "red lead").

Thermogravimetric analysis showed this reaction to begin with a weight loss at 400°C (Fig. 1, curve A) with a total loss of 34.4 ± 0.5% giving support to the postulated acid–base/oxidation reaction

$$3PbSO_4 + 6NO_3^- \rightarrow Pb_3O_4 + 3SO_4^{2-} + 6NO_2 + O_2 \qquad (1)$$

(calculated weight loss = 33.8%).

Lead(II) nitrate is also very soluble (> 0.3 m at 280°C) and again was not observed to react until 450°C when nitrogen dioxide was evolved. Thermogravimetry showed the first weight loss at 420°C but the highest rate of loss, found at 490°C (Fig. 1, curve B), was at a higher temperature than when this compound was heated alone (Fig. 1, curve C), indicating some stabilisation by coordinating nitrate anions, as has been frequently found with other cations in nitrate melts. To avoid weight loss due to melt decomposition, heating was continued isothermally at 490°C, the overall weight loss being 31.9 ± 0.9% corresponding to the overall equation

$$Pb(NO_3)_2 \rightarrow PbO + 2NO_2 + \tfrac{1}{2}O_2 \qquad (2)$$

(calculated weight loss = 32.6%).

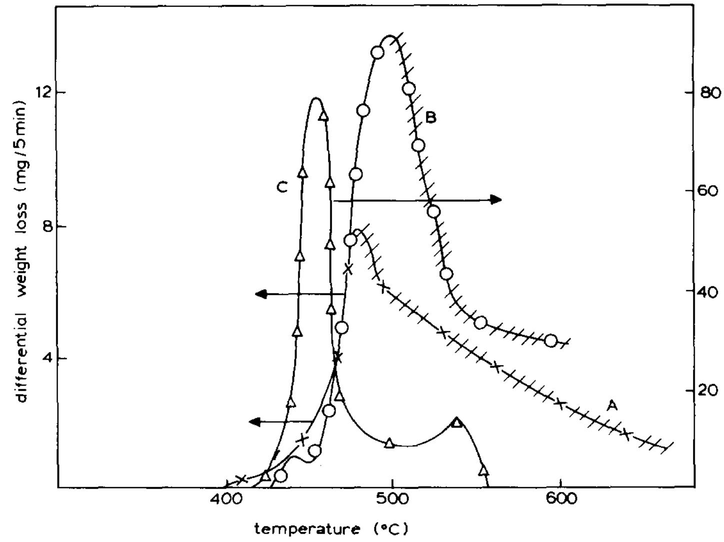

Fig. 1. Thermogravimetric analysis of lead(II) compounds. Curve A (×) $PbSO_4$ (0.34 *m*) in $LiNO_3/KNO_3$; curve B (○) $Pb(NO_3)_2$ (0.23 *m*) in $LiNO_3/KNO_3$; curve C (△) $Pb(NO_3)_2$ (0.70 g).

The red solid formed by the end of this reaction was shown to be lead(II) oxide by quantitative analysis (found: Pb, 91.2; calc. for PbO: Pb, 92.8%) and confirmed (as red tetragonal PbO) by X-ray powder diffraction. It is considered that the absence of a separate maximum weight loss for the intermediate formation of red lead, as was found when lead(II) nitrate was heated alone (Fig. 1, curve C, first weight loss 28.0 ± 0.6%, second weight loss 4.6 ± 0.2%, final product PbO 91.2 ± 0.9% Pb) was due partly to the higher temperature of reaction caused by cation stabilisation in the melt but mainly because of the availability of nitrite produced by the thermal equilibrium

$$NO_3^- \rightleftharpoons NO_2^- + \tfrac{1}{2}O_2 \tag{3}$$

whilst the melt was kept at 490°C for 6 h, thus reducing any red lead formed

$$3Pb(NO_3)_2 \rightarrow Pb_3O_4 + 6NO_2 + O_2 \tag{4}$$

$$Pb_3O_4 + NO_2^- \rightarrow 3PbO + NO_3^- \tag{5}$$

Equations (3), (4) and (5) of course are equivalent to eqn. (2).

In contrast to certain other cations (e.g., zinc(II) [19] and cobalt(II) [20]) lead(II) was not much stabilised by the presence of added halide ions (see Fig. 2, curves A, B and C) even at ratios as high as 20 : 1 (see Fig. 2, curve D). Nor was much change caused by added potassium sulphate at 2 : 1 ratio (Fig. 2, curve E) though the weight loss started ~ 30°C higher than with a 1 : 1 ratio (Fig. 1, curve A) which may indicate some stabilisation.

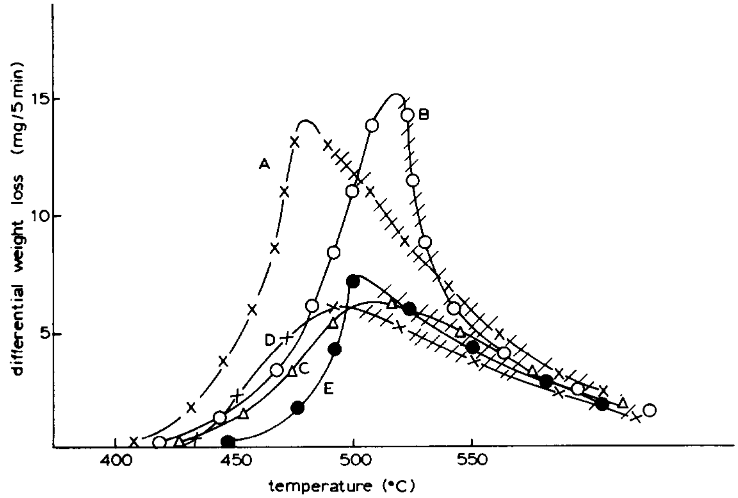

Fig. 2. Thermogravimetric analysis of lead(II) nitrate in lithium nitrate–potassium nitrate eutectic. Curve A (×) $PbNO_3$ (0.34 *m*) and KF (1.03 *m*); curve B (○) $PbNO_3$ (0.32 *m*) and KCl (0.92 *m*); curve C (△) $PbNO_3$ (0.33 *m*) and KBr (1.00 *m*); curve D (+) $PbNO_3$ (0.41 *m*) and KCl (8.22 *m*); curve E (●) $PbNO_3$ (0.29 *m*) and K_2SO_4 (0.58 *m*).

The reaction of lead(II) nitrate in the melt containing added potassium nitrite took place at much lower temperatures (Fig. 3, curve A) as expected in view of the much greater basicity of such solutions [21], the two maxima on the weight loss curve representing some intermediate stabilisation. The overall loss (21.9%) indicated that nitrite ions were the principal reactants in accordance with the equation

$$Pb(NO_3)_2 + 2NO_2^- \rightarrow PbO + 2NO_3^- + NO_2 + NO \qquad (6)$$

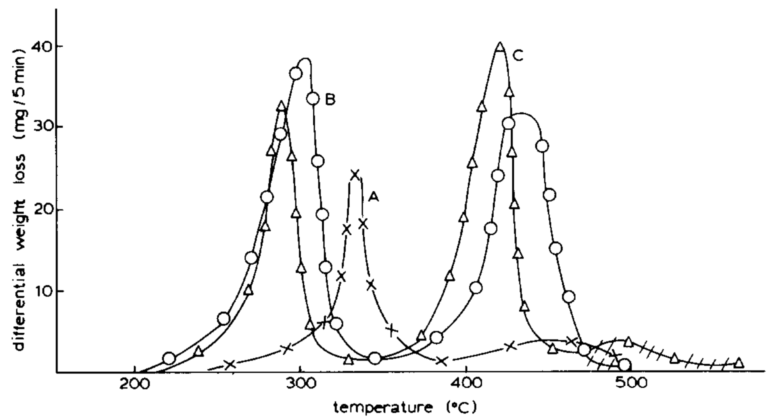

Fig. 3. Thermogravimetric analysis in lithium nitrate–potassium nitrate eutectic. Curve A (×) $Pb(NO_3)_2$ (0.68 *m*) and KNO_2 (1.44 *m*); curve B (○) $Pb(NO_3)_2$ (0.19 *m*) and $NaPO_3$ (0.59 *m*); curve C (△) $NaPO_3$ (0.84 *m*).

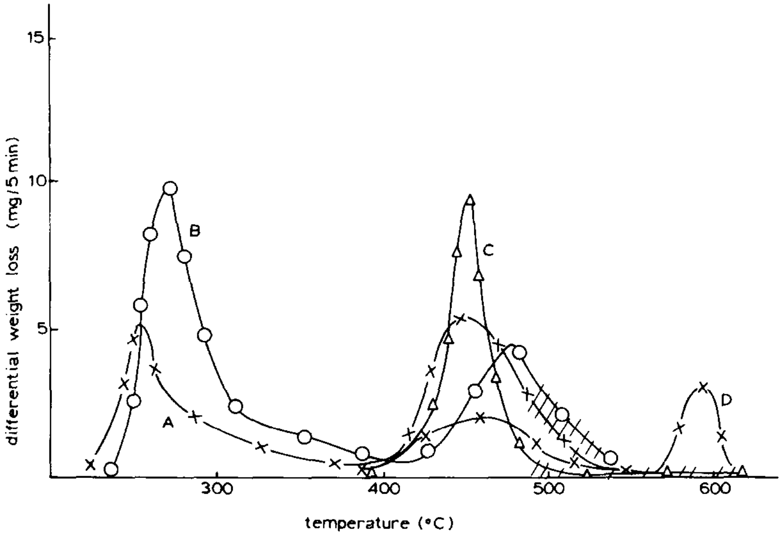

Fig. 4. Thermogravimetric analysis of lead(II) compounds. Curve A (×) $PbCO_3$ (0.44 *m*) in $LiNO_3/KNO_3$; curve B (○) $2PbCO_3 \cdot PbO$ (0.21 *m*) in $LiNO_3/KNO_3$; curve C (△) PbO_2 (0.47 *m*) in $LiNO_3/KNO_3$; curve D (+) PbO_2 (0.30 g).

(calculated weight loss = 22.8%) which has previously been shown to describe the reaction in pure nitrite melts [17]. The low weight loss was not compatible with the intermediate formation of red lead, nor with nitrate acting as the source of oxide ions (cf. eqn. 2).

Addition of a Lux-Flood acid ($NaPO_3$) to lead(II) nitrate in melt caused little change, the reaction occurring in two stages very similar to those when no lead(II) was present (Fig. 3, curves B and C) and incidentally indicated no additional stabilisation of lead(II) by ortho- or pyrophosphate anions (the reaction products of $NaPO_3$ [18]).

Lead(II) carbonate reacted in the melt with weight loss starting at 230°C (Fig. 4, curve A), the loss of 5.7 ± 0.3% by 350°C corresponding to the formation of a basic carbonate ($2PbCO_3 \cdot PbO$, "white lead").

$$3PbCO_3 \rightarrow 2PbCO_3 \cdot PbO + CO_2 \qquad (7)$$

(calculated weight loss = 5.5%).

The same product had been reported earlier when lead(II) carbonate reacted in potassium nitrate at 350–415°C [22]. However, in the eutectic melt a further reaction commenced at 350°C with a weight loss of 8.5 ± 0.4% to 500°C when a red solid was formed and shown to be red lead by X-ray powder diffraction.

$$2PbCO_3 \cdot PbO + \tfrac{1}{2}O_2 \rightarrow Pb_3O_4 + 2CO_2 \qquad (8)$$

(calculated weight loss = 8.9%).

No evidence for such a reaction in potassium nitrate was reported in the course of potentiometric titrations with potassium dichromate [22].

Basic lead(II) carbonate ($2PbCO_3 \cdot Pb(OH)_2$) reacted in a rather similar fashion (Fig. 4, curve B), the almost completely insoluble compound becoming yellow at 250°C when it started to lose weight to 400°C with a 8.4 ± 0.5% loss. The white insoluble material formed when the reaction was stopped at 300°C (well after the maximum rate of loss) gave *d* spacings of 4.40(35), 4.05(40), 3.98(10), 3.63(20), 3.58(20), 3.33(100), 3.26(75), 2.96(85), 2.80(90) and 2.61(80), which did not correspond to any compound in the JCPDS Index, but which is considered to be a basic carbonate.

$$2PbCO_3 \cdot Pb(OH)_2 \rightarrow PbCO_3 \cdot 2PbO + H_2O + CO_2 \qquad (9)$$

(calculated weight loss = 8.0%). The melt became brown above 400°C and a further weight loss occurred (3.8 ± 0.2%) corresponding to the formation of red lead which was confirmed by X-ray powder diffraction.

$$PbCO_3 \cdot 2PbO + \tfrac{1}{2}O_2 \rightarrow Pb_3O_4 + CO_2 \qquad (10)$$

(calculated weight loss = 3.6%).

Lead(II) oxide when heated with the melt did not dissolve but darkened in colour to a reddish-brown at 470°C, though on cooling to room temperature it changed back to yellow. No weight losses were observed and the final product was shown to be orthorhombic lead(II) oxide by X-ray powder diffraction and the stoichiometry confirmed by quantitative analysis. Red lead was also shown to be stable when heated to 500°C, with no weight loss or change of colour. However, black lead(IV) oxide did react in the melt becoming a dark violet colour at 480°C (changing to red on cooling to room temperature) with a weight loss of 4.5 ± 0.5% (Fig. 4, curve C) corresponding to the formation of red lead which was again confirmed by X-ray powder diffraction (3.38(100), 3.11(20), 2.91(50), 2.78(45), 2.63(30), 2.03(10), 1.97(10), 1.91(20) and 1.82(20)).

$$3PbO_2 \rightarrow Pb_3O_4 + O_2 \qquad (11)$$

(calculated weight loss = 4.5%). This reaction is identical with that found when lead(IV) oxide was heated alone (Fig. 4, curve D) though the temperature range of the latter was somewhat wider and a further weight loss occurred at higher temperatures of 2.2 ± 0.5%, corresponding to the formation of lead(II) oxide.

$$Pb_3O_4 \rightarrow 3PbO + \tfrac{1}{2}O_2 \qquad (12)$$

(calculated weight loss = 2.2%).

Thus the stability of red lead found in the nitrate melt at temperatures up to 500°C would seem to be largely due to not having reached the decomposition temperature. However, it was reduced on long heating (e.g., 6 h at 490°C with $Pb(NO_3)_2$), probably by the action of nitrite formed by thermal dissociation (eqns. 3 and 5), to lead(II) oxide. There was certainly no evidence of oxidation of lead(II) oxide to higher oxides as had been hypothesised in potassium nitrate [22], nor was there any support for the suggestion [15] that lead(IV) oxide was formed by oxidation of lead by molten nitrate above 475°C. These latter authors reported three nitrate melts ($NaNO_3$, KNO_3 and $(NaK)NO_3$) to cause this oxidation but the change to larger, less acidic, cations will only (slightly) reduce the oxidizing power of the nitrate. These authors also state that there was no "spontaneous precipitation" of *any* lead oxide in lithium nitrate–potassium nitrate, a finding at variance with the present results and also surprising in view of the frequently verified facts that Lux-Flood acids react at lower temperatures in this melt than in the less acidic sodium nitrate–potassium nitrate eutectic [18,23], thus lead(II) would be expected to form insoluble oxides at least as readily in lithium nitrate–potassium nitrate (the authors' assertion [15] that the non-precipitation of lead oxides is due to the formation of LiO^- [24], is of course not a complete explanation since the self ionisation of nitrate, although not yet measured in melts other than $NaNO_3/KNO_3$, would be expected to vary somewhat with the alkali metal cation [25]). Both Salaha et al. [15] and the present work do agree, however, that red lead is the initial product at 350–475°C. The basic nitrate ($5PbO \cdot Pb(NO_3)_2$) found [15] below 350°C with oxide/lead(II) ratios of < 1.5 (in $NaNO_3/KNO_3$) differs from the 1 : 1 ratio reported by Bombi and Fiorani [11] when lead(II) was titrated with electrolytically generated oxide in equimolar sodium nitrate–potassium nitrate.

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