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# MOLTEN NITRATE EUTECTICS: THE REACTION OF FOUR LANTHANIDE CHLORIDES

D.A. HABBOUSH *, D.H. KERRIDGE and S.A. TARIQ **
*Department of Chemistry, The University, Southampton (Gt. Britain)*

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## ABSTRACT

The reactions of lanthanum(III), cerium(III), praseodymium(III) and europium(III) chlorides have been studied in the molten lithium nitrate–potassium nitrate and sodium nitrate–potassium nitrate eutectics. The ultimate reaction products have been shown to be oxides ($La_2O_3$, $CeO_2$, $Pr_6O_{11}$ and $Eu_2O_3$, respectively) which increased the rate of decomposition of the melts, while in three cases an intermediate oxide nitrate was formed ($LaONO_3$, $PrONO_3$ and $EuONO_3$). The temperatures and stoichiometries of the reactions have been established.

## INTRODUCTION

The chemistry of most elements in molten nitrates is now moderately well understood [1], with the notable exception of the lanthanides where very little has been reported since the review of 1972 [2] which listed those separation processes that had been investigated, i.e. solvent extraction into an organic phase and ion exchange on zeolite or glass fibre paper, together with polarography and visible–UV spectroscopy.

Because these physical methods require stable solutions of lanthanides, all that can be deduced about reaction chemistry is that lanthanide(III) cations are generally stable up to 250°C in lithium nitrate–potassium nitrate [3], to 326°C in sodium nitrate–potassium nitrate [4] and to 360°C in potassium nitrate [5]. Virtually the only chemical reactions hitherto reported in nitrate melts are the instability of cerium(IV) nitrate in lithium nitrate–potassium nitrate producing a precipitate and nitrogen dioxide [6], the precipitation of lanthanide fluorocarbonates in sodium nitrate and potassium nitrate [7], and the precipitation of 'double vanadates', probably potassium lanthanide tetravanadates, from potassium nitrate [8].

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* Present address: Department of Chemistry, State University of New York, Buffalo, NY, U.S.A.

** Present address: Department of Inorganic and Analytical Chemistry, La Trobe University, Australia.

Thus the thermal stability ranges of four lanthanide chlorides were investigated, as were the products formed on reaction with the melt, and the stoichiometry of the Lux-Flood acid–base and oxidation–reduction reactions involved.

## EXPERIMENTAL

### *Materials*

The nitrate eutectics were prepared as previously reported [9]. Lanthanide chlorides were obtained as follows: $LaCl_3$ hydrate 99.9% (Rare Earth Products Ltd.), $CeCl_3$ hydrate (BDH), $Pr_6O_{11}$ (BDH), $Eu_2O_3$ (BDH), the latter two oxides being dissolved in hydrochloric acid and the chloride crystallised. All the chlorides were dehydrated with thionyl chloride [10] and analysed for chloride by Volhard's method (found (%): Cl, 43.2, 43.4, 42.9, 40.9%; calcd. for Cl in $LaCl_3$, $CeCl_3$, $PrCl_3$, $EuCl_3$: 43.4, 43.2, 43.0, 41.2%, respectively).

### *Measurements*

Thermogravimetry was carried out on a Stanton TR-1 thermobalance as previously reported [9]. Aqueous insoluble products were extracted from the solidified melt with water, washed, dried, weighed and analysed. Lanthanum and cerium were estimated by EDTA titration, praseodynium spectrophotometrically at 392 nm after conversion to the chloride, and europium after heating to 800°C was weighed as $Eu_2O_3$ [11].

Electronic absorption spectra were measured using a Unicam SP800 for aqueous solutions, an SP700 with reversed optics for melt solutions, and an SP1700 with an SP850 reflectance attachment for solidified melts. Infrared spectra were taken of products pressed into potassium bromide discs on an SP200 spectrometer.

X-Ray diffraction was carried out with a Unicam 19 cm camera of Debye–Scherrer type using zirconium filtered molybdenum or nickel filtered Cu$K_\alpha$ radiation from a General Electric XRD 6 generator.

## RESULTS AND DISCUSSION

Lanthanum(III) chloride dissolved slowly in sodium nitrate–potassium nitrate eutectic at 250°C to give a colourless solution which became turbid after 45 min. On increasing the temperature, reaction occurred above 370°C producing a white precipitate. After heating the reaction mixture to 680°C the water-insoluble product gave the X-ray powder diffraction lines of lanthanum(III) oxide (found: La 85.1%; calcd. for $La_2O_3$: La 85.3%). A white silky precipitate, also insoluble in water, was obtained after 56 h at 400°C, but with a different analysis (found: La 63.5%; calcd. for $LaONO_3$: La 64.0%) and a different diffraction pattern [2.93 (vs), 2.08 (s), 1.78 (s), 1.64 (s), ASTM Index for $LaONO_3$, 2.92 (90), 2.06 (100), 2.02 (80), 1.81 (100), 1.72 (90)].

Thermogravimetry also showed two reactions (Fig. 1, curve A), the first with a maximum around 500°C giving an average weight loss to the minimum at 540°C of 47.0% which is close to that calculated for the formation of lanthanum oxide nitrate.

$$LaCl_3 + 3\,NO_3^- \rightarrow LaONO_3 + 3\,Cl^- + 2\,NO_2 + \tfrac{1}{2}\,O_2 \tag{1}$$

(calcd. weight loss 44.0%)

This product had IR absorptions at 715, 725, 830, 1090, 1445 $cm^{-1}$, close to those of nitrate in lanthanum(III) nitrate hexahydrate [12], i.e. 720, 740; 825; 1090; 1370, 1450 $cm^{-1}$ attributed to the $\nu_4$, $\nu_2$, $\nu_1$ and probably $\nu_3$ vibrations, respectively. However, the total weight loss to 680°C (186%) was much larger than calculated for the Lux-Flood acid–base reaction (66.1%; eqn. (2)]

$$2\,LaCl_3 + 6\,NO_3^- \rightarrow La_2O_3 + 6\,Cl^- + 6\,NO_2 + \tfrac{3}{2}\,O_2 \tag{2}$$

due to thermal decomposition of the nitrate melt. This decomposition appeared to be catalysed by the lanthanum(III) oxide produced since the rate of decomposition is much higher than that of the pure eutectic (compare curves A and B, Fig. 1).

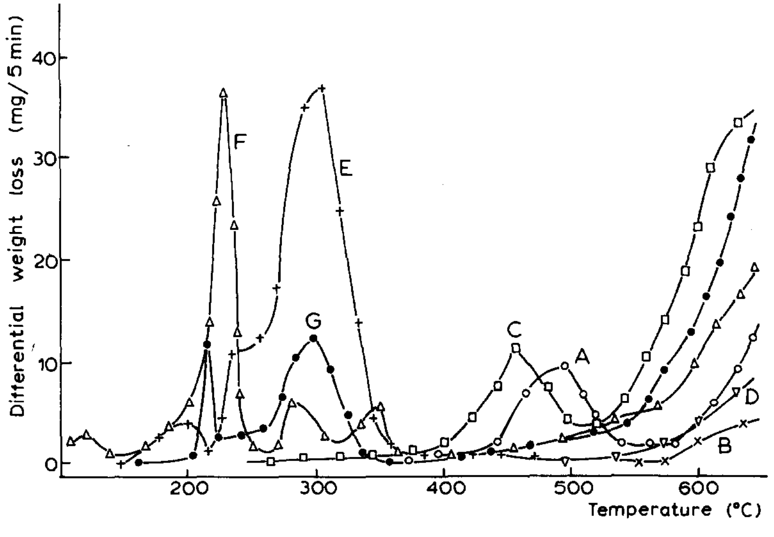

Fig. 1. Thermogravimetry of lanthanide(III) chlorides in molten nitrate eutectics. Curve A (○ - ○ - ○) 0.23 m $LaCl_3$ in $NaNO_3/KNO_3$; B(× - × - ×), pure $NaNO_3/KNO_3$; C(□-□-□), 0.22 m $LaCl_3$ in $LiNO_3/KNO_3$; D(▽-▽-▽), pure $LiNO_3/KNO_3$; E(+ - + - +) 0.73 $CeCl_3$ in $NaNO_3/KNO_3$; F(△-△-△), 0.15 m $CeCl_3$ in $NaNO_3/KNO_3$; G(●-●-●), 0.23 m $CeCl_3$ in $LiNO_3/KNO_3$.

The reaction in lithium nitrate–potassium nitrate was similar; lanthanum(III) chloride dissolved slowly at 150°C, becoming faintly turbid after 75 min. Precipitation increased with time, particularly on the glass surfaces. Much white solid formed after 20 h at 400°C (found: La 64.3%) while X-ray diffraction showed the sesquioxide was formed at 650°C. The pure oxide nitrate has been reported to decompose to the sesquioxide at 520–580°C [13]. Once again thermogravimetry (Fig. 1, curve C) showed two reactions. The first attributed as before to lanthanum oxide nitrate formation [eqn. (1)] with a weight loss to the minimum at 500°C averaging 49.9%, both the temperatures of the maximum rate of loss and of the minimum were lower than in sodium nitrate–potassium nitrate, as expected and in line with the generally lower reactivity of the latter eutectic shown in a number of acid–base reactions [9]. The second reaction (weight loss 327% to 650°C) again showed a faster weight loss than in the pure melt (Fig. 1, curve D), again indicating catalysis of the melt decomposition.

Cerium(III) chloride dissolved in sodium nitrate–potassium nitrate eutectic to give a yellow solution at 250°C which became turbid on increasing the temperature to 275°C and evolved nitrogen dioxide at 300°C. A yellow precipitate, formed after 14 h at 300°C, or in 3.5 h at 470°C, which was shown to be cerium(IV) oxide by X-ray diffraction, also by analysis (found: Ce 80.7%; calcd. for $CeO_2$: Ce, 81.5%) and in confirmation was soluble in hydrochloric acid when hydrogen peroxide was present. Thermogravimetry also indicated the formation of this oxide, the average weight loss to 400°C being 60.3% close to that given in eqn. (3).

$$CeCl_3 + 3\ NO_3^- \rightarrow CeO_2 + 3\ Cl^- + 3\ NO_2 + \tfrac{1}{2}\ O_2 \qquad (3)$$

(calcd. weight loss 62.5%)

Cerium(IV) oxide is the expected product at these temperatures, being formed on heating cerium(III) nitrate hexahydrate to 450°C [14] and cerium(III) formate or oxalate to 360°C [15,16]. The temperature of maximum rate of weight loss varied with concentration from 310°C at 0.73 m (Fig. 1, curve E) to 230°C at 0.15 m (where a shoulder was observed at higher concentrations (Fig. 1, curve F) suggesting that chloro complexes may be formed during the latter part of the reaction of large amounts of cerium(III) chloride, resulting in stabilisation of cerium and thus higher reaction temperatures. Again the oxide product appears to catalyse the melt decomposition (compare curves F and B in Fig. 1). Similar reactions were found in lithium nitrate–potassium nitrate eutectic, cerium(III) chloride slowly dissolving at 150°C and giving some turbidity after 10 h at 190°C. Nitrogen dioxide was detected and a yellow precipitate formed after 15 h at 200°C. Thermogravimetry on a solution of intermediate concentration (Fig. 1, curve G) showed nearly equal maxima both at slightly lower temperatures than with the less reactive eutectic [weight loss to 360°C 59.7%, (found: Ce

80.3%), cf. eqn. (3)], and again with a more rapid decomposition at higher temperatures than in the pure melt (Fig. 1, curve D).

In lithium nitrate–potassium nitrate eutectic praseodymium(III) chloride dissolved to give a clear pale green solution which at 200°C gave four absorption bands: 22400 cm$^{-1}$ (2.6 l mole$^{-1}$ cm$^{-1}$), 21200 (1.4), 20600 (1.0), and 16900 (0.6), which are characteristic of Pr$^{3+}$ and closely similar to those reported in this melt at 150°C, but as frequently found for molten salt lanthanide spectra the molar extinction coefficients (values in parentheses) were distinctly lower than the values reported for aqueous solutions. Similar bands were found in the reflectance spectrum of the solidified solution. A green solution was also formed in sodium nitrate–potassium nitrate eutectic at 250°C which was stable for at least 16 h. However, at higher temperatures, e.g. 440°C, a slow precipitation of a pale green solid occurred, becoming a colourless melt after 24 h. At a still higher temperature (500°C) this precipitate became black after 2 h. The latter was shown to be the higher oxide $Pr_6O_{11}$ (found: Pr 82.5%; calcd. for $Pr_6O_{11}$: Pr 82.8%) and in total was 69.7% of the weight of the original chloride (calcd. for formation of $Pr_6O_{11}$ from $PrCl_3$ 68.8%). Once more the oxide produced appeared to catalyse the melt decomposition but to an even greater extent (cf. Fig. 2, curves A and B). The intermediate pale green precipitate, which gave the X-ray diffraction lines of neither oxide ($Pr_6O_{11}$ nor $Pr_2O_3$), the *d* values being 3.64 (s), 3.45 (s), 3.21 (s), 3.00 (s), 2.25 (s), 2.05 (m), 1.81 (m), 1.64 (w), corresponded to an average weight loss of 46.3% to the minimum at 510°C, which was close to

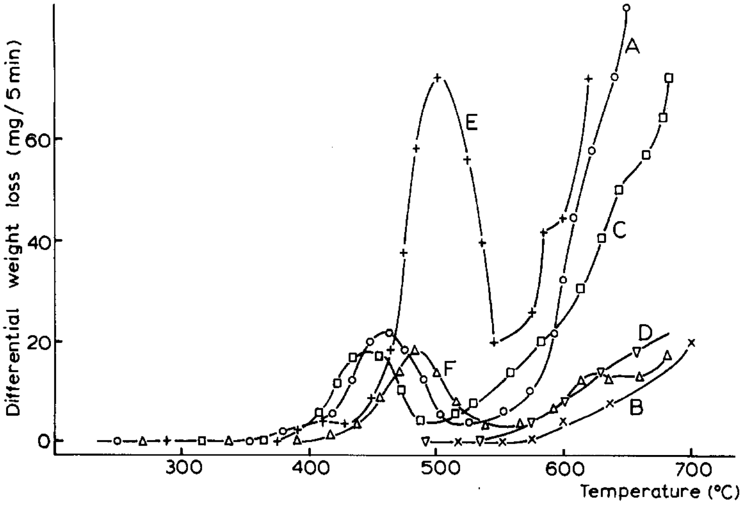

Fig. 2. Thermogravimetry of lanthanide(III) chlorides in molten nitrate eutectics. Curve A(○-○-○), 0.18 $PrCl_3$ in $NaNO_3/KNO_3$; B(× - × - ×), pure $NaNO_3/KNO_3$; C(□-□-□), 0.21 $PrCl_3$ in $LiNO_3/KNO_3$; D(▽-▽-▽), pure $LiNO_3/KNO_3$; E(+ - + - +), 0.23 m $EuCl_3$ in $LiNO_3/KNO_3$; F(△-△-△), 0.22 m $EuCl_3$ in $NaNO_3/KNO_3$.

that expected for the formation of the oxide nitrate

$$PrCl_3 + 3\ NO_3^- \rightarrow PrONO_3 + 3\ Cl^- + 2\ NO_2 + \tfrac{1}{2}\ O_2 \qquad (4)$$

(calcd. weight loss 43.7%)

Thermogravimetry in lithium nitrate–potassium nitrate gave a similar weight loss (48.7% average) to the minimum at 490°C (Fig. 2, curve C), and again the weight loss to 680°C (~ 160%) was far larger than that calculated for the formation of the black higher oxide found, i.e.

$$6\ PrCl_3 + 18\ NO_3^- \rightarrow Pr_6O_{11} + 18\ Cl^- + 18\ NO_2 + \tfrac{7}{2}O_2 \qquad (5)$$

(calcd. weight loss 63.3%)

suggesting catalysis of nitrate thermal decomposition (cf. Fig. 2, curve D).

Europium(III) chloride dissolved in lithium nitrate–potassium nitrate eutectic at 200°C giving four absorption bands [25200 $cm^{-1}$, 0.6 l $mole^{-1}$ $cm^{-1}$, 23900 (0.1), 21500 (0.5) and 18600 (0.1)] which were similar in position and molar extinction coefficient to those reported by Carnall et al. [17]; analogous bands were found in the reflectance spectrum of the quenched solution. Solutions in both nitrate melts began to lose weight at 360°C (Fig. 2, curves E and F) with a maximum at 480–490°C, the average weight loss to the minima at 550°C (i.e. 40.2% in $NaNO_3/KNO_3$ and 42.8% in $LiNO_3/KNO_3$) being close to that for the formation of the oxide–nitrate [eqn. (6)]

$$EuCl_3 + 3\ NO_3^- \rightarrow EuONO_3 + 3\ Cl^- + 2\ NO_2 + \tfrac{1}{2}O_2 \qquad (6)$$

(calcd. weight loss 41.8%)

though the high temperature of this reaction may suggest an alternative reaction. It will be recalled that in sodium nitrate–potassium nitrate, lanthanum(III) chloride reacted with a maximum rate at 490°C and praseodymium(III) chloride a little lower at 470°C (in each case in lithium nitrate–potassium nitrate the maxima were at temperatures 20–40°C lower, illustrating the greater reactivity of the latter melt, as has been found with many other reactants [9], and attributed to the effect of the highly polarising lithium cation). The slightly lower reaction temperature with praseodymium is the effect expected of decreasing cation size (due to the lanthanide contraction) with consequent increase in Lux-Flood acidity. The very considerably lower temperature of reaction of cerium(III) chloride found here (cf. curves E, F and G of Fig. 1) cannot, however, be explained on this basis, but suggests the presence of the more highly acidic cerium(IV). Such cations could have been produced by oxidation in the nitrate melt and as well as being considerably more acidic, would also form stronger chloro complexes, which could give rise to the stabilisation effect found with more concentrated solutions and mentioned earlier.

Finally, to return to the much higher reaction temperature found with europium(III) chloride than would have been predicted from its smaller cation size and consequently higher acidity [i.e. suggesting a reaction temperature below that of praseodymium(III)], europium has a comparatively stable lower oxidation state and this could be formed by the increasing concentration of nitrite resulting from displacement of the equilibrium of thermal decomposition of the melt, i.e.

$$NO_3^- \rightleftharpoons NO_2^- + \tfrac{1}{2}\,O_2 \tag{7}$$

as the temperature increased. This effect of thermally produced nitrite would be analogous to the reduction of permanganate, periodate and iodate previously found [18,19] [europium(II) has also been postulated in pure nitrite melts [20]].

If this hypothesis is correct, the intermediate compound may be a europium(II) oxide nitrate, e.g.

$$2\,EuCl_3 + 6\,NO_3^- \rightarrow Eu_2O(NO_3)_2 + 6\,Cl^- + 4\,NO_2 + \tfrac{3}{2}\,O_2 \tag{8}$$

where the calculated weight loss of 44.8% is also reasonably close to those of the minima. However, chemical analysis of the precipitate (found: Eu 64.8% in $NaNO_3/KNO_3$, 64.4% in $LiNO_3/KNO_3$; calcd. for $EuONO_3$: Eu 66.1%; calcd. for $Eu_2O(NO_3)_2$: Eu 68.4%) was closer to the value expected for the europium(III) oxide nitrate, and it is possible that this oxidation could have occurred during the washing and drying of the intermediate product. Infrared of the intermediate product gave sharp absorptions at 1095, 1120 and 1218 $cm^{-1}$ (the first probably being the $\nu_1$ vibration of nitrate, the two latter closer to oxide bands).

A second weight loss followed when a pale yellow insoluble oxide was produced (found: Eu 83.6% in $NaNO_3/KNO_3$, 83.9% in $LiNO_3/KNO_3$; calcd. for $Eu_2O_3$: Eu 86.4%), which had five of the X-ray diffraction lines of europium(III) oxide. Variable catalysis of the melt decomposition was observed in the presence of this oxide as the weight loss in sodium nitrate–potassium nitrate was closely similar to that of the pure melt (Fig. 2, curve B) but equal to that with lanthanum(III) oxide in lithium nitrate–potassium nitrate.

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