MOLTEN NITRITE EUTECTICS: THE REACTION OF FOUR LANTHANIDE(III) CHLORIDES

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ABSTRACT

Cerium(III) chloride reacted with sodium nitrite–potassium nitrite eutectic, initially in the solid state but more rapidly on melting, to form cerium(IV) oxide, while lanthanum(III) chloride, praseodymium(III) chloride and europium(III) chloride reacted, very largely in the liquid state, undergoing anion exchange and a partial Lux–Flood acid–base reaction to form oxide nitrites ($LnONO_2$) initially. At higher temperatures the latter two chlorides reacted further to form the oxides (Pr_6O_{11} and Eu_2O_3, respectively). In lithium nitrite–potassium nitrite eutectic, the course of the reactions was similar but the temperatures at which reaction commenced were lower.

INTRODUCTION

Relatively little investigation has yet been reported in molten nitrites, as compared to molten nitrates, but a brief review [1] has appeared and the chemistry is understood at least in outline. However, nothing has yet been published on the reaction of any lanthanide compounds in nitrite melts despite their evident interest. Since besides Lux–Flood acid–base reactions of lanthanide cations lead to formation of oxide species, it would also be anticipated that nitrite could act as an oxidizing agent as well as a reductant. Indeed with some transition metal compounds [of V(V) and Cr(VI)] it has been shown that reduction to an intermediate of lower oxidation state can occur before a re-oxidation to the final product [2,3]. Nitrite anions also have the property of coordinating to transition metal cations as either nitro or nitrito ligands (i.e., via N or O). Mixed complexes have also been demonstrated by IR and visible spectroscopy [4].

In view of these many possibilities the chemistry of four lanthanide (III) chlorides was investigated in two alkali metal nitrite eutectics.

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EXPERIMENTAL

Materials

Sodium nitrite–potassium nitrite and lithium nitrite–potassium nitrite eutectics were prepared as described previously [4]. 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 crystallized. All the chlorides were dehydrated with thionyl chloride [8] and analyzed 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).

Procedure

Visually observed reactions and thermogravimetric analysis were carried out as described previously (refs. 4 and 3, respectively). X-Ray diffraction was carried out with a Unicam 19 cm camera of Debye–Scherrer type using zirconium filtered molybdenum radiation from a General Electric XRD6 generator. The experimental d-spacing and intensities were compared with those for that compound listed in the ASTM Index. Infrared spectra were taken of powdered water-washed and dried products, pressed into thin discs with potassium bromide, on a Perkin–Elmer 225 spectrometer.

The lanthanides were analyzed gravimetrically by heating to constant weight in air at 900°C and weighing as La_2O_3, CeO_2, Pr_6O_{11} and Eu_2O_3, respectively. The weights of the solid products, intermediate and final, after complete extraction with water and drying, are reported as a percentage of that of the original chloride used in the reaction.

Quantitative analysis of nitrate in solidified reacted melts was carried out by Leithe's method as described in detail elsewhere [3]. This determination was necessary with every thermogravimetric analysis as a variable amount of the nitrogen dioxide initially formed reacted as

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \tag{1}$$

Thus the experimental weight loss was increased by an amount calculated from the amount of nitrate formed. Intermediate weight losses were increased by a proportional amount.

RESULTS AND DISCUSSION

When lanthanum(III) chloride was added to sodium nitrite–potassium nitrite eutectic at 250°C there was an immediate reaction with evolution of nitrogen dioxide and nitric oxide. A white precipitate was formed in the still

yellow melt, but no further reaction was observed. The washed and dried precipitate analyzed with the same stoichiometry as that of the oxide nitrite previously prepared from aqueous solutions [5]. (Found: La 68.8%; calcd. for $LaONO_2$: La 69.1%. The total weight of this precipitate was, on average, 81.8% of the original weight of lanthanum(III) chloride. Calcd. for formation of $LaONO_2$ from $CaCl_3$ is 81.9%.) Thermogravimetric analysis (Fig. 1, curve A) showed weight loss to start slightly below the melting point of the pure eutectic (i.e. 220°C) but probably when a solution formed, with a maximum rate of loss at 230°C. The total loss was 30.9% after correction for formation of nitrate, which agrees closely with that expected from the equation
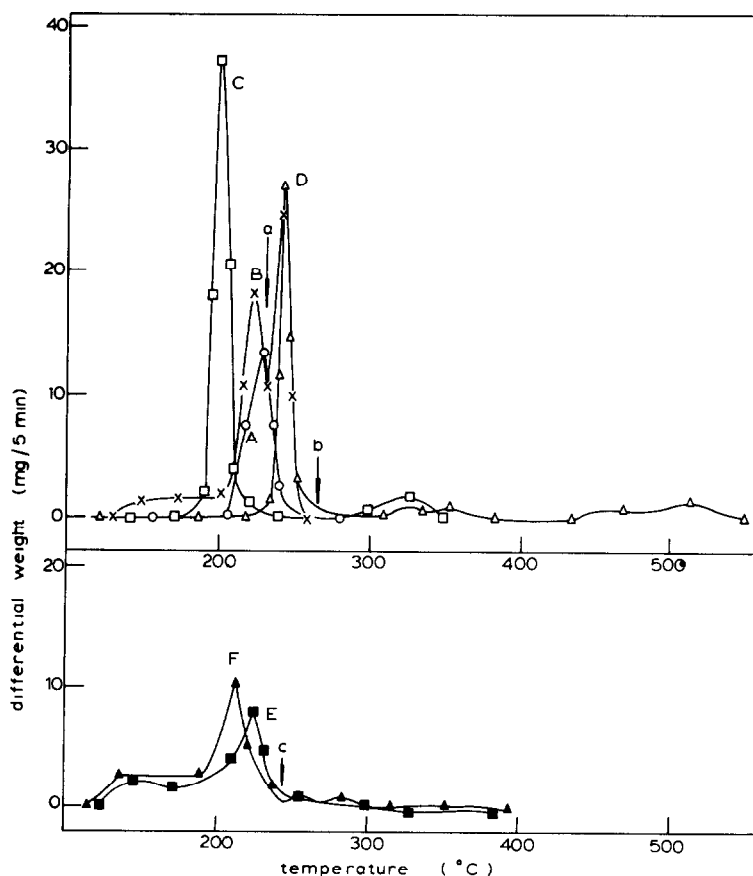
$$LaCl_3 + 3\,NO_2^- \rightarrow LaONO_2 + 3\,Cl^- + NO_2 + NO \tag{2}$$
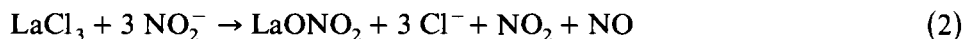
(calcd. weight loss 31.0%)

Fig. 1. Thermogravimetric analysis of lanthanide(III) chlorides in molten nitrite eutectics. Curve A (–O–O–), 0.24 m $LaCl_3$ in $NaNO_2/KNO_2$ eutectic; B (– × – × –), 0.33 m $CeCl_3$ in $NaNO_2/KNO_2$ eutectic; C (–□–□–), 0.38 m $PrCl_3$ in $NaNO_2/KNO_2$ eutectic; D(–△–△–), 0.29 m $EuCl_3$ in $NaNO_2/KNO_2$ eutectic; E(–■–■–), 0.35 m $PrCl_3$ in $LiNO_2/KNO_2$ eutectic; F (–▲–▲–), 0.42 m $EuCl_3$ in $LiNO_2/KNO_2$ eutectic.

TABLE 1

Infrared absorption bands of lanthanide oxide nitrites produced by reaction of $LnCl_3$ with $NaNO_2/KNO_2$

Reactant	Assignment to nitro ligand transitions (cf. Nakamoto [6]) (cm^{-1})		
	$\nu_a(NO_2)$	$\nu_s(NO_2)$	$\delta(ONO)$
$LaCl_3$	1418(s)	1365(s)sh	874(m)
	1478(s)		874(m)
$PrCl_3$	1438(s)	1360(s)sh	834(m)
	1493(s)		879(m)
$EuCl_3$	1418(s)	1365(s)sh	879(m)
	1498(s)		

The IR bands shown by the product to 650 cm^{-1} accord most closely with nitrite bonded as a nitro ligand, rather than as nitrito or an ionic nitrite, and are given in Table 1 with the assignments of Nakamoto [6].

Cerium(III) chloride also reacted with the eutectic immediately at 250°C, again to give the brown gases and a milky yellow suspension which settled to give a white precipitate after 30 min. This white solid gave the X-ray diffraction lines of cerium(IV) oxide [3.14(vs), 2.75(m), 1.91(s), 1.64(s), 1.60(w), 1.38(w), 1.27(m), 1.23(m), 1.12(w). ASTM Index for CeO$_2$, 3.12(100), 2.71(29), 1.91(51), 1.63(44), 1.35(5), 1.24(15), 1.10(12), 1.04(9)], a satisfactory analysis (found: Ce 80.6; calcd. for CeO$_2$: Ce 81.4%), and the expected weight of product, an average of 68.4% (calcd. for CeO$_2$ from CeCl$_3$: 69.8%). Thermogravimetric analysis showed reaction to begin well below the melting point of the eutectic (Fig. 1, curve B) and to have two maxima on the weight loss curve. The overall loss (of 39.2–43.4%) became, after correction for nitrate formation 43.9% on average, which was close to that for the equation

$$CeCl_3 + 3\ NO_2^- \rightarrow CeO_2 + 3\ Cl^- + NO_2 + 2\ NO \qquad (3)$$
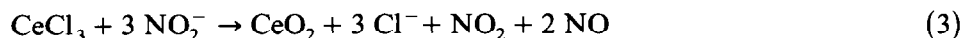
(calcd. weight loss 43.0%)

The weight loss to the minimum around 235°C (marked 'a' on curve B of Fig. 1) averaged 33.6% after correction, which may indicate that an oxide nitrite (i.e., CeONO$_2$) was an intermediate. [Calcd. for loss of 2 N + 3 O per CeCl$_3$, cf. eqn. (2): 30.8%. Formation of cerium(IV) oxide nitrite; e.g. CeO(NO$_2$)$_2$, is less likely, as the calculated loss for NO per CeCl$_3$ is only 8.8%.] Alternatively the double peak in the weight loss curve may indicate stabilization, probably of cerium (IV), by the formation of chloro complexes, analogous to that already found for zinc [7], iron [8] and cobalt [9] and postulated in the reaction of cerium(III) chloride with nitrate melts [10]. In lithium nitrite–potassium nitrite eutectic (m.p. 98°C) reaction was well underway by 130°C when brown gas was evolved and a thick yellow suspension formed.

Praseodymium(III) chloride also reacted immediately in sodium nitrite–potassium nitrite eutectic at 250°C giving off nitrogen dioxide and forming a green solution with a yellow foam on top. A green-white solid slowly separated over 7 h and was shown to be the oxide nitrite (found: Pr 69.2; calcd. for $PrONO_2$: Pr 69.4%; and weight of product 81.7%; calcd. for $PrONO_2$ from $PrCl_3$: 82.1%) which had the IR absorption maxima listed in Table 1, as well as bands at 1086(m), 734(s) and 714(s) cm^{-1} which may be due to the presence of some oxide nitrate.

Further heating of the green solution to 375°C caused a brown-black precipitate to form, which was shown to be the higher oxide by analysis (found: Pr 82.2; calcd. for Pr_6O_{11}: Pr 82.8%) and weight of product (68.4%, calcd. for Pr_6O_{11} from $PrCl_3$: 68.8%) though the X-ray diffraction pattern [d-values 3.21(vs), 2.87(w), 2.33(m), 1.96(s), 1.91(m), 1.68(s)] only included the three strongest lines in the ASTM Index for this oxide [3.19(100), 1.94(80), 1.66(80)]. Thermogravimetric analysis (Fig. 1, curve C) showed two separate temperatures of reaction, the first beginning below the melting point with a maximum close to 200°C. The weight loss to 230°C of 32.9% after correction for nitrate formation also gave support to formation of an oxide nitrite [calcd. for loss of 2 N + 3 O per $PrCl_3$, cf. eqn. (2): 30.7%]. The second weight loss began at 240°C and finished at 350°C, the overall loss being 40.0% after correction for nitrate formation.

$$6 \; PrCl_3 + 18 \; NO_2^- \rightarrow Pr_6O_{11} + 18 \; Cl^- + 7 \; NO_2 + 11 \; NO \tag{4}$$
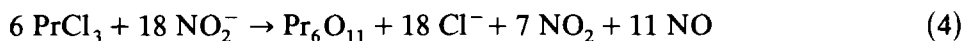
(calcd. weight loss 44.0%)

In the lithium nitrite–potassium nitrite melt reaction began at 120°C (Fig. 1, curve E) again evolving brown gas and forming a green solid after 1 h at 160°C, while at higher temperatures a black solid was formed. Thermogravimetry showed the weight loss to 245°C (i.e., after the rapid reaction) to be 35.9%, and the overall loss to be 44.6% (both after correction for nitrate formation). The latter loss again supported the formation of the stable oxide, as did the analyses (found: Pr 80.9; Calcd. for Pr_6O_{11}: Pr 82.8%; weight of product 66.4%; calcd. for Pr_6O_{11} from $PrCl_3$: 68.8%), with the oxide nitrite as the probable intermediate.

Europium(III) chloride reacted in a similar way with both nitrite eutectics. Thermogravimetry showed the weight loss to occur from 220°C in sodium nitrite–potassium nitrite, with a maximum at 245°C, the corrected loss to 265°C ('b' on curve D of Fig. 1) being an average of 31.0% (calcd. for loss of 2 N + 3 O per $EuCl_3$: 29.4%). The formulation of the cream coloured product as an oxide nitrite was supported by the analysis (found: Eu 72.9; calcd. for $EuONO_2$: Eu 71.0%) and the weight of product (80.7%; calcd. for $EuONO_2$ from $EuCl_3$: 82.8%). The IR bands, again suggesting nitro groups, are shown in Table 1. Reaction continued at higher temperatures as a distinct second stage with formation of an insoluble product, also cream

coloured, which was shown to be europium(III) oxide by X-ray diffraction, quantitative analysis (found: Eu 84.9; calcd. for Eu_2O_3: Eu 86.4%) and from the weight of product formed (69.3%; calcd. from formation of Eu_2O_3 from $EuCl_3$: 68.1%). The overall weight loss of 44.5% after correction agreed with the reaction

$$2\, EuCl_3 + 6\, NO_2^- \rightarrow Eu_2O_3 + 6\, Cl^- + 3\, NO_2 + 3\, NO \tag{5}$$

(calcd. weight loss 44.1%)
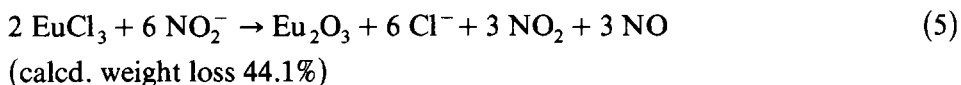
In the lithium nitrite–potassium nitrite melt, reaction began at a much lower temperature (Fig. 1, curve F) though with a closely similar total loss (of 44.3% after correction) and an intermediate loss to 'c' of 37.9% after correction for nitrate formation.

With sodium nitrite–potassium nitrite the very much lower initial reaction temperature of cerium(III) chloride suggests the formation of cerium(IV), which as a more acidic cation should give a lower reaction temperature even with the solid state nitrite (oxidation by air is unlikely as cerium(III) chloride is stated to be stable to 260°C [11]). The reaction temperature of praseodymium with respect to that of lanthanum decreased as expected with the decreasing cation size and hence increasing Lux–Flood acidity. However, the higher reaction temperature found with europium(III) chloride may indicate some reduction to the more stable and less acidic europium(II). Indeed if the intermediate product were of this oxidation state [i.e., $Eu_2O(NO_2)_2$] the analyses expected (73.9% Eu, a product weighing 79.8% of original $EuCl_3$ and a weight loss of 32.4%, i.e., 2 N + 3.5 O per $EuCl_3$) are rather closer to those found. Substitution of lithium nitrite–potassium nitrite eutectic demonstrated that the commencement of reaction was at considerably lower temperatures as would be expected in an already liquid phase, but otherwise the maximum reaction rate temperatures appeared to be similar, suggesting that even with the former eutectic the melting point had been decreased sufficiently by reactants (of products) that reaction then was very largely in the liquid state.

The intermediate formation of an oxide nitrite can be paralleled by the reaction of lanthanide(III) chlorides with molten nitrates when oxide nitrates were initially formed [10]. However, in the latter melts the reaction temperatures were considerably higher, illustrating the much higher basicity and also oxidizing/reducing power of nitrite melts, as has been found previously (compare ref. 12 with refs. 8 and 9).

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