Thermochimica Acta, 84 (1985) 13–18
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MOLTEN LITHIUM CARBONATE–SODIUM CARBONATE–POTASSIUM CARBONATE EUTECTIC: THE REACTION OF FOUR LANTHANIDE(III) CHLORIDES

D.A. HABBOUSH *, D.H. KERRIDGE and S.A. TARIQ **

Department of Chemistry, The University, Southampton (Gt. Britain)

(Received 6 August 1984)

ABSTRACT

Cerium(III) chloride reacted with carbonate in the solid state under a carbon dioxide atmosphere, to form cerium(IV) oxide, while europium(III) chloride, praseodymium(III) chloride and lanthanum(III) chloride underwent anion exchange and partial decomposition to give the dioxymonocarbonates initially. The latter three compounds took up carbon dioxide as the temperature increased, the amount varying in accordance with the basicity of the cations ($\frac{1}{8}$, $\frac{1}{2}$ and 1 mole of CO_2 per mole of $Ln_2O_2CO_3$, respectively), as did the temperatures of reaction.

INTRODUCTION

Molten carbonate chemistry is of considerable interest, both in its own right and also because of its practical uses (for many years in metal surface treatment and potentially in fuel cells). Thus, some understanding of the behaviour of a number of main group elements has been built up (see ref. 1 for a review of work in equimolar Li_2CO_3/Na_2CO_3, which is close to the eutectic composition) and latterly particularly of transition metals both in the equimolar melt [1] and in the ternary eutectic [2,3]. However, up to the present, no work has been published concerning the reactions of lanthanide compounds.

Therefore, four readily available lanthanide(III) chlorides were chosen for this investigation from the early lanthanide series, which showed a range of basicity and, in the case of cerium, the possibility of a ready change of oxidation state. The carbonates, potentially formed by anion exchange in the melt, are known to be somewhat unstable on heating [4]. The normal

---

* Present address: Department of Chemistry, Sacred Heart University, Bridgeport, CT, U.S.A.

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

carbonates, always obtained as hydrates from aqueous solution, thermally decompose losing both water and carbon dioxide and form a series of basic carbonates of which the most stable is the dioxymonocarbonate ($Ln_2O_2CO_3$, or $Ln_2O_3CO_2$ or Ln_2CO_5) [5,6]. The same basic carbonates are produced by the thermal decomposition of oxalates, and a thorough study by Turcotte et al. [7] using thermogravimetry, X-ray diffraction and IR spectroscopy has shown that these basic carbonates can exist in three polymorphic forms with different thermal stabilities.

EXPERIMENTAL

Materials

The carbonate eutectic was prepared as previously described [2]. Lanthanide chlorides were obtained as follows: $LaCl_3$ hydrate, 99.9% (Rare Earth Products Limited), $CeCl_3$ 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 [8] and analysed for chloride by Volhard's method (Found; Cl, 43.2, 43.4, 42.9, 40.9%; calc. for $LaCl_3$, $CeCl_3$, $PrCl_3$, $EuCl_3$: 43.4, 43.2, 43.0, 41.2%, respectively).

Procedure

Thermogravimetric analyses, X-ray powder diffraction and IR measurements were carried out as previously described (refs. 2, 3 and 2, respectively). The weight of the final solid product, after complete extraction with water and drying, is reported as a percentage of the original chloride taken. Praseodymium was analysed gravimetrically as Pr_6O_{11} after heating to constant weight in air to 750°C.

RESULTS AND DISCUSSION

Cerium(III) chloride reacted with ternary carbonate eutectic in the solid state. Thermogravimetry showed the weight loss to begin at 155°C (Fig. 1, curve A) and to reach a maximum rate at 240 and 320°C, with a small minimum around 280°C. The weight loss ended at 340–350°C when the final product was shown to be cerium(IV) oxide by X-ray powder diffraction (*d* values: 3.14(s), 2.93(w), 2.81(w), 2.70(w), 1.91(m), 1.64(m), 1.58(w), 1.24(w), 1.21(w), 1.11(w), 1.04(w). ASTM Index for CeO_2: 3.12(100), 2.71(29), 1.91(51), 1.63(44), 1.24(15), 1.10(12), 1.04(9), with the two strongest lines of lithium carbonate (2.83(100), 2.93(95)) which proved very difficult to wash from this product) though the average overall weight loss of 27.0% was not very close to that expected for the following equation

$$2CeCl_3 + 3CO_3^{2-} \rightarrow 2CeO_2 + 6Cl^- + 2CO_2 + CO \qquad (1)$$

(Calculated weight loss, 23.5%). However, the solid product was not soluble in strong mineral acids unless hydrogen peroxide was present, a characteristic property of cerium(IV) oxide.

The formation of the most stable oxide, in this case involving an oxidation to cerium(IV), was the exception among the four lanthanide chlorides because the lanthanide(III) oxides, formed when the higher oxide was unstable, were considerably more basic and combined even with weakly acidic carbon dioxide, both in the initial and the final products, as shown by thermogravimetry.

The least basic lanthanide(III) cation, as europium(III) chloride, was found to commence reaction slowly with carbonate from 250 to 280°C, losing weight at a faster rate from 350°C and with a maximum at 380–390°C (Fig. 1, curve B). A very slight gain in weight (average 1.2%) occurred at higher temperatures, from 450 to 550°C. The average loss to 450°C was 17.4%, with the nett loss to 550°C thus being 16.2%. The final product had an X-ray powder diffraction pattern (3.54(s), 3.21(w), 2.93(vs), 2.65(m), 2.08(w), 1.99(s), 1.88(w), 1.78(w), 1.64(w), 1.58(w), 1.29(w), 1.25(2), 1.22(w)) which could not be matched to any listed europium compound, and certainly not to europium(III) oxide, though the *d* values of the strongest lines of both

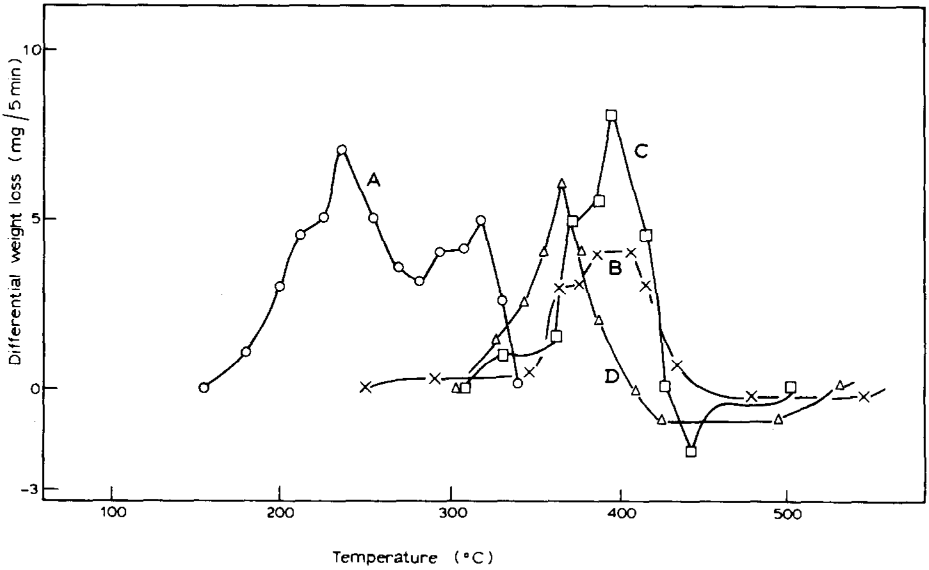

Fig. 1. Thermogravimetric analysis of lanthanide(III) chlorides in $Li_2CO_3/Na_2CO_3/K_2CO_3$ ternary eutectic. (A) ○, 0.35 M $CeCl_3$; (B) ×, 0.36 M $EuCl_3$; (C) □, 0.30 M $PrCl_3$; (D) △, 0.83 M $LaCl_3$.

$Eu_2O_2CO_3$ (2.92) and of "europium carbonate" (3.53), were present. The IR spectrum (Table 1) showed the presence of carbonate in the final product, and the weight loss to 450°C was consistent with the intermediate formation of the most familiar basic carbonate, i.e.

$$2EuCl_3 + 3CO_3^{2-} \rightarrow Eu_2O_2CO_3 + 6Cl^- + 2CO_2 \qquad (2)$$

(calculated weight loss 17.0%) by anion exchange and partial decomposition, the dioxymonocarbonate then apparently combining with carbon dioxide (approximately $\frac{1}{8}CO_2$ per $Eu_2O_2CO_3$) to give a stoichiometry close to $Eu_2O_{1\,7/8}(CO_3)_{1\,1/8}$ (calculated weight loss for formation from $EuCl_3$, 16.0%). The weight of the water-washed and dried final product (74.1% of that of the original $EuCl_3$) is also close to those calculated for these stoichiometries (for $Eu_2O_{1\,7/8}(CO_3)_{1\,1/8}$ 77.7%, and for $Eu_2O_2CO_3$ 76.6%).

The reaction of praseodymium(III) chloride began at the slightly higher temperature of 300°C (Fig. 1, curve C), as would be expected for a slightly less acidic cation than europium(III), with a weight loss which reached a maximum rate at 390°C, then falling quite rapidly to zero, followed by a gain in weight beginning near 420°C and ending at 500°C. The X-ray powder diffraction lines of this green final product (3.54(s), 3.29(m), 3.00(vs), 2.70(m), 2.15(w), 2.05(m), 1.91(w), 1.83(w), 1.76(w), 1.68(w), 1.62(w), 1.46(w), 1.39(w), 1.33(w), 1.29(w), 1.24(w)) did not match those of praseodymium(III) oxide, nor those of Pr_6O_{11}, and though the IR absorptions (Table 1) showed the presence of carbonate, only one line was close to those given for Pr_2CO_5 (the strongest, 2.97). This was not unexpected since the weight loss to 420°C was on average 16.1%, and slightly less than that for the equation

$$2PrCl_3 + 3CO_3^{2-} \rightarrow Pr_2O_2CO_3 + 6Cl^- + 2CO_2 \qquad (3)$$

(calculated weight loss 17.8%) while the overall loss was 13.6% indicating a larger gain that was found with europium and close to that for the formation of $Pr_2O_{1\,1/2}(CO_3)_{1\,1/2}$ (calculated weight loss from $PrCl_3$, 13.3%). The quantitative analysis was consistent with this (found: Pr, 71.3. Calc. for

TABLE 1

IR absorption bands of final products of $LnCl_3$ reactions with carbonate

Reactant	Assignment to unidentate carbonate bands (cf. Nakamoto [9]) (cm^{-1})					
	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_5(B_2)$	$\nu_6(B_2)$	$\nu_8(B_1)$
$EuCl_3$		1095		1480 1535		855
$PrCl_3$	1360	1085	722	1420 1466 1525	667	855
$LaCl_3$		1083		1457 1505	666	854

$PrCl_3$: Pr, 71.2%) as was the total weight of the final product, found to be 81.5% of weight of original $PrCl_3$ (calc. for $Pr_2O_{1\,1/2}(CO_3)_{1\,1/2}$, 80.0%). It is interesting to note that Turcotte et al. [7] reported that "only the dioxymonocarbonates of lanthanum and praseodymium (of the 12 lanthanides studied) decomposed reversibly within the times allowed".

Finally, the most basic cation, lanthanum(III) as the chloride, was found to commence reaction at 300°C but with a lower temperature of maximum reaction rate (on average 360°C) and the lowest temperature at which the weight gain began (390°C average). The gain was also the largest (6.4% average) of the cations investigated. The final creamy-white product again clearly showed the presence of carbonate by the IR spectra (Table 1), but the X-ray powder pattern (3.54(s), 3.29(w), 3.00(s), 2.70(w), 2.15(w), 2.05(m), 1.94(w), 1.83(w), 1.70(w), 1.64(w), 1.34(w), 1.30(w)) did not agree with that for $La_2O_2CO_3$ (except for a fairly similar strongest line, of 3.02) nor with that for La_2O_3. The overall weight loss of 9.8% was, however, reasonably close to that calculated for the formation of $La_2O(CO_3)_2$ (9.0%), as was the total weight of the product 87.5% of the initial weight of $LaCl_3$ (calc. for $La_2O(CO_3)_2$, 84.4%). The intermediate product formed with a weight loss of 16.3% was again apparently analogous to that formed in eqns. (2) and (3) (calc. weight loss from $LaCl_3$, 17.9%).

To sum up, the trends in temperatures of reaction with carbonate eutectic and of absorption of carbon dioxide were those expected from the well-known variation in basicity of the cations, with little effect being found on the melting of the carbonate eutectic (except that curves B and C both had maxima there which may indicate a faster reaction in the liquid state), the very different behaviour of cerium being due to its ease of oxidation. The much lower initial reaction temperature of cerium(III) chloride, characteristic of a much more acidic cation, would be consistent with the initial formation of cerium(IV) by oxidation with carbon dioxide. The overall similarity of the IR absorptions of the final products suggested that the variable take up of carbon dioxide ($\frac{1}{8}$ to 1 mol CO_2 per $Ln_2O_2CO_3$) had been largely in "interstitial" positions which have had little effect on the overall symmetry, a suggestion which is supported by the generally similar X-ray patterns. The actual values of the IR absorptions are closest to unidentate rather than to bidentate carbonate, in the subdivision of Nakamoto [9] (see assignments in Table 1), though they may be better assigned as all being of Type 1 (tetragonal) crystal structure as defined by Turcotte et al. [7] (isostructural with $Bi_2O_2CO_3$).

ACKNOWLEDGEMENTS

Grateful thanks are extended to the University of Basrah, Iraq, and to La Trobe University, Australia, for grant of sabbatical leave (to D.A.H. and S.A.T., respectively).

REFERENCES

1 J.A. Plambeck, Fused Salt Systems, Vol. X of Encyclopaedia of Electrochemistry of the Elements, M. Dekker, New York and Basel, 1976.
2 D.A. Habboush, D.H. Kerridge and S.A. Tariq, Thermochim. Acta, 28 (1979) 143.
3 D.A. Habboush and D.H. Kerridge, Thermochim. Acta, 44 (1981) 151.
4 C. Duval, Inorganic Thermogravimetric Analysis, 2nd edn., Elsevier, Amsterdam, 1963.
5 T. Moeller, The Chemistry of the Lanthanides, Pergamon Texts in Inorganic Chemistry, Vol. 26, Pergamon, Oxford, 1975.
6 R.L.N. Sastry, S.R. Yoganarasimhan, P.N. Mehrotra and C.N.R. Rao, J. Inorg. Nucl. Chem., 28 (1966) 1165.
7 R.P. Turcotte, J.O. Sawyer and L. Eyring, Inorg. Chem., 8 (1969) 238.
8 J.H. Freeman and M.L. Smith, J. Inorg. Nucl. Chem., 7 (1958) 224.
9 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.