Thermal stability and solubility of alkaline earth nitrates and chromates in nitrate melts

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Abstract

Calcium nitrate precipitates calcium oxide at 620°C in lithium nitrate–potassium nitrate eutectic, but is less reactive in sodium nitrate–potassium nitrate eutectic. Strontium and barium nitrates are still less reactive, in accordance with the trend in Lux–Flood acidity.

Solubility values were determined for these nitrates and for calcium and potassium chromates. Latent heat of fusion values were derived for the latter two compounds.

INTRODUCTION

Little has so far been published on the chemistry of Group IIa elements in molten nitrates. Of the lightest element, the beryllium(II) cation has been briefly referred to as a Lux–Flood acid [1] and to form chloro complexes in sodium nitrate–potassium nitrate eutectic [2].

The heavier cations have been chromatographed on glass fibre [3], have been exchanged on zeolites [4] from molten nitrates and their Raman [5] and IR spectra studied, the latter indicating stronger chloro than nitrato complexes for calcium, but not for magnesium [6]. Solubilities of magnesium oxide [7], magnesium, calcium and barium chromates [8] and calcium nitrate [9] have been reported, the latter (at approx. 7.5 M) probably too high by comparison with correlations derived from quasi-lattice and ideal solubility equations [10]. Lastly, the reaction temperatures and products of metallic magnesium and calcium have been established [11].

This meagre amount of information suggested the value of a comparative study of compounds of the three heavier elements (Ca, Sr, Ba) as an extension to the survey of the chemistry of magnesium compounds previously published [12].

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EXPERIMENTAL

Materials

Lithium nitrate–potassium nitrate eutectic was prepared as described previously [12]; the sodium nitrate–potassium nitrate eutectic was prepared in an analogous fashion. Anhydrous calcium nitrate (BDH reagent grade) was dried at 180°C for 16 h, potassium chromate (Reagent grade) at 180°C for 9 h, strontium and barium nitrates (Reagent grades) at 200°C for 14 h.

Methods

Thermogravimetric analyses were carried out with a Stanton TR-1 thermobalance using 10 ml silica crucibles, with a heating rate of $2°C \, min^{-1}$. The results are reported as a percentage weight loss, calculated on the weight of the specified reactant, and graphically represented as the differential weight loss (mg per 5 min) against temperature.

The solubilities of the more soluble nitrates were determined by the visual method, whereas those of the sparingly soluble calcium chromate were estimated by analysis of samples of melt solution drawn into a heated tube through a glass wool plug [13]. Calcium was determined quantitatively by EDTA titration using murexide indicator, and chromate by titration with iron(II) using barium diphenylamine sulphonate indicator.

RESULTS AND DISCUSSION

Anhydrous calcium nitrate dissolved readily in lithium nitrate–potassium nitrate eutectic and showed no visible signs of decomposition below 500°C, but solutions became yellow above this temperature and evolved gas. A white precipitate formed at 620°C, which, after washing and drying, contained 69.2% calcium (Calc. Ca in CaO, 71.5% Ca). Thermogravimetry showed weight loss from 490°C (Fig. 1, curve A), but this was quantitatively small (e.g. 0.5% after 70 min at 500°C) though greater than that of the melt alone (cf. curves A and B, Fig. 1). Additions of sodium nitrite to the melt solution, up to a maximum $Ca:NO_2^-$ ratio of 1:6 respectively, did not increase the rate of weight loss, although addition of nitrite (more basic than nitrate) reduces the reaction temperatures of transition metal cations [14].

In sodium nitrate–potassium nitrate eutectic, calcium nitrate behaved qualitatively similarly, but the colour changed to yellow and a gas was
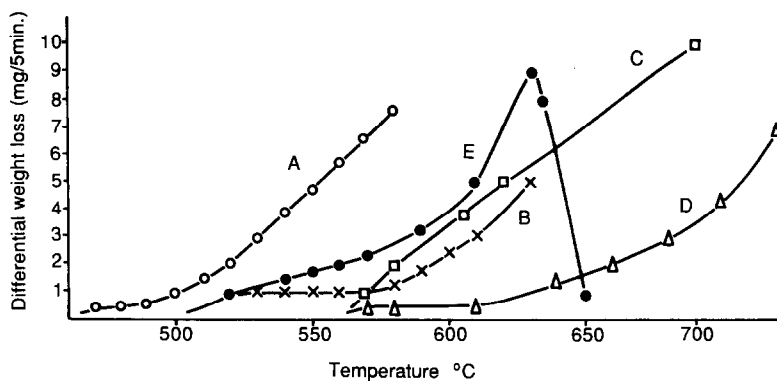
Fig. 1. Thermogravimetric analysis of alkaline earth cations in nitrate melts: curve A, 2.06 m Ca(NO$_3$)$_2$ in LiNO$_3$–KNO$_3$ eutectic; curve B, LiNO$_3$–KNO$_3$ eutectic alone; curve C, 0.20 m Ca(NO$_3$)$_2$ in NaNO$_3$–KNO$_3$ eutectic; curve D, NaNO$_3$–KNO$_3$ eutectic alone; curve E, 0.85 g Ca(NO$_3$)$_2$.

evolved at ≤560°C. Thermogravimetric analysis (Fig. 1, curve C) also showed less rapid reaction, again illustrating the greater polarising power, and hence greater reactivity, of the small lithium cation. Comparison with the thermal decomposition of calcium nitrate without melt (Fig. 1, curve E), which decomposed at lower temperatures than when dissolved in sodium nitrate–potassium nitrate eutectic, showed the stabilising effect of coordination of calcium cations by additional nitrate anions, a feature already observed with transition metal (Co(II) [13], Cu(II) [15]) and 'p block' metal cations (Ga(III) [16], In(III) [17], Pb(II) [18], Bi(III) [19]). However, this stabilisation was more than counterbalanced by the presence of the polarising lithium cations in lithium nitrate–potassium nitrate eutectic solution (cf. curves A and E, Fig. 1). Figure 1 curve E also shows that pure calcium nitrate had decomposed completely by 650°C with a total weight loss of 66.0 wt.%, corresponding to the equation

$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + 0.5O_2 \tag{1}$$

(Calc. for loss of 2N + 5O per Ca(NO$_3$)$_2$ 65.8%), the white residue after decomposition analysing as 70.0% Ca.

Determination of solubilities indicated values of 0.4 and 0.7 molal (m) at 150 and 330°C respectively in the lithium nitrate–potassium nitrate eutectic and approximately 0.12 m at 250°C in sodium nitrate–potassium nitrate eutectic, much smaller values than that claimed earlier [9] and more in accord with values expected from the correlation of calculated solubilities and other experimental values for other solutes [10]. Calcium chloride was more soluble, approximately 2.2 and 5.0 m at 360 and 430°C respectively.

Strontium nitrate dissolved in lithium nitrate–potassium nitrate eutectic (0.78 m at 450°C) to give more stable solutions which showed no weight

loss up to 500°C by thermogravimetry. Nor was any weight loss found when sodium nitrite was dissolved in the nitrate eutectic, at $NaNO_2/Sr(NO_3)_2$ ratios of 3:1 and 6:1. However, without melt, strontium nitrate alone decomposed from 550°C with a total weight loss of 50.8%, corresponding to

$$Sr(NO_3)_2 \rightarrow SrO + 2NO_2 + 0.5O_2 \qquad (2)$$

(Calc. for loss of $2N + 5O$ per $Sr(NO_3)_2$ 51.0%).

Barium nitrate also dissolved ($0.78\,m$ at 420°C in $LiNO_3$–KNO_3 eutectic) without any colour change or weight loss up to 500°C, when melt decomposition began. This trend towards higher decomposition temperatures with increasing size of alkaline earth cation, bearing in mind that the reaction temperature of magnesium nitrate in lithium nitrate–potassium nitrate is 400°C [12], is expected, and in accord with the trend in Lux–Flood acidity that has previously been found for the Group IIIa cations and other series.

Calcium chromate was formed on mixing an equivalent solution of potassium chromate with calcium nitrate solution in lithium nitrate–potassium nitrate eutectic. The solubility was low so it precipitated at 200°C and was determined quantatively by estimation of filtered samples taken over time from thermostated solutions (Fig. 2). Both the calcium and chromate concentrations were closely similar and showed equilibrium values to be reached in 4 h. This solubility is an order of magnitude higher than that reported in sodium nitrate–potassium nitrate eutectic [8], but gives support to the claim that its solubility is much greater than that of magnesium chromate [8], an apparent reversal of the order found for aqueous solubilities.
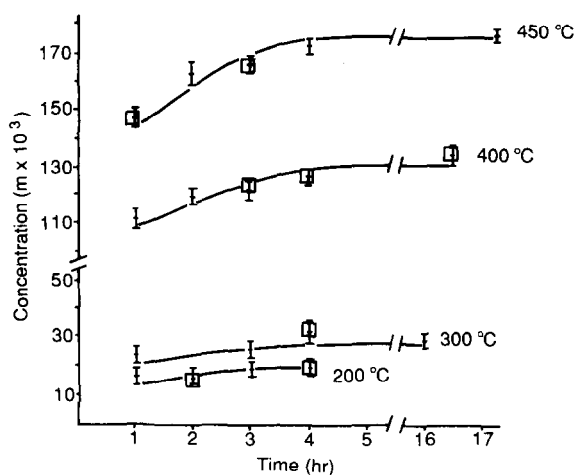

Fig. 2. Variation of calcium chromate solubility in $LiNO_3$–KNO_3 eutectic with time: ꜰ indicates calcium; □ indicates chromate (in filtered samples).
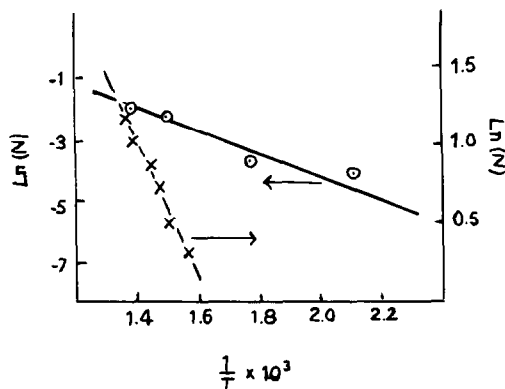
Fig. 3. Variation with temperature of solubilities of calcium chromate ($\bigcirc$) left hand scale, and potassium chromate ($\times$) right hand scale (N_1 = mole fraction).

Use of the ideal solubility equation

$$-RT \ln N_1 = L_f(1 - T/T_m) \tag{3}$$

where R is the gas constant, N_1 the mole fraction of solute at temperature T, and L_f and T_m the latent heat of fusion and melting point respectively of the solute, gave a value of 7.60 kcal mol^{-1} for the latent heat of fusion of calcium chromate.

In contrast, the solubility of potassium chromate was larger (Fig. 3) but gave a value of 7.90 kcal mol^{-1} for the latent heat, which was higher than the value of 7.54 kcal mol^{-1} determined earlier by DTA. Using the last value gave calculated solubilities 39–55% lower than experimental (average 45%). Both chromate solutions in nitrate eutectic were stable with no weight loss to 500°C, nor visual sign of decomposition, though the yellow solutions darkened to red.

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