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MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC: THE REACTION OF COMPOUNDS OF INDIUM

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ABSTRACT

The reaction of indium(III) nitrate, chloride and sulphate in molten nitrate has been shown by thermogravimetric analysis to be of the Lux–Flood acid–base type, the insoluble product being indium(III) oxide. The temperature of reaction has been shown to increase with coordination of added anionic ligands to the indium (i.e. causing stabilisation), the relative effect being $F^- > SO_4^{2-} > Cl^- > IO_3^- > ClO_4^- > NO_3^-$. However, additions of potassium nitrite, chlorate or bromide caused similar reactions to that of nitrate alone but at lower temperatures because they behave as stronger Lux–Flood bases, in the case of bromide by catalysing the nitrate–nitrite equilibrium.

INTRODUCTION

Very little information has so far been published on the behaviour of indium compounds in molten nitrates. The two known facts have both been derived from electrochemical studies; the first states that indium(III) sulphate was only sparingly soluble in the ternary lithium nitrate–sodium nitrate–potassium nitrate at 160 °C and gave no polarographic waves [1]; the second is that indium(III) chloride gave a yellow precipitate in sodium nitrate–potassium nitrate eutectic at 245 °C, which was thought to possibly be "indium(III) oxide chloride" though no analysis was quoted [2].

In view of this scarcity of information a systematic investigation of the chemistry of indium in molten lithium nitrate–potassium nitrate eutectic was carried out, with emphasis on the formation of complexes.

EXPERIMENTAL

Lithium nitrate–potassium nitrate eutectic was prepared as previously described [3]. Potassium chloride, potassium bromide, potassium chlorate and potassium iodate (all AnalaR), potassium nitrite and potassium perchlorate (both LR grade) were dried for 2 h at 110 °C. Potassium sulphate

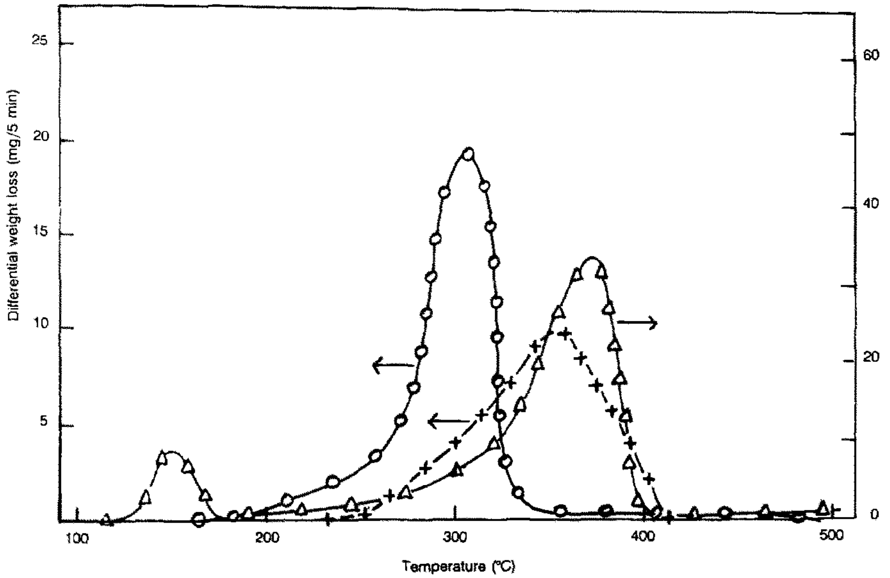

Fig. 1. Thermogravimetric analysis of indium(III) salts in lithium nitrate-potassium nitrate eutectic: curve A, o, 0.66 M indium(III) nitrate (left hand scale); curve B, +, 0.59 M indium(III) chloride (left hand scale); curve C, △, 0.39 M hydrated indium(III) sulphate (right hand scale).

(AnalaR) was dried at 200 °C for 2 h. Potassium fluoride, anhydrous indium(III) chloride and hydrated indium(III) sulphate (all LR) were used as received. Hydrated indium(III) nitrate (LR) (found: In, 31.5%; NO_3^-, 49.6%) was dehydrated in the molten eutectic to avoid hydrolysis, at 150 °C (solubility > 1.5 M (molal)) on a rotary pump. Dehydration was monitored by the weight loss and verified by quantitative analysis of the melt solution for indium. The time required increased with concentration; for example, a 0.4 M solution required 2 h.

Qualitative reactions, thermogravimetric analysis, solubility determinations and X-ray powder diffraction were carried out as previously described [3].

RESULTS AND DISCUSSION

Dehydrated solutions (0.6 M) of indium(III) nitrate in nitrate eutectic began to lose weight at 180 °C (Fig. 1, curve A) with a maximum rate of weight loss at 305 °C. The total weight loss was 53.8 ± 0.4%, close to that expected from the reaction

$$2In(NO_3)_3 \rightarrow In_2O_3 + 6NO_2 + 1\tfrac{1}{2}O_2 \qquad (1)$$

$$(\text{Calc. for loss of } 3N + 7\tfrac{1}{2}O \text{ per } In(NO_3)_3 \ 53.9\%)$$

The yellow solid remaining after water extraction of the quenched melt and drying, was analysed for indium (found: In 82.2%, calc. for In_2O_3, In 82.7%).

Anhydrous indium(III) chloride had a limited solubility in the nitrate eutectic (~ 0.2 M at 180 °C), but reacted at higher temperatures, nitrogen dioxide being evolved from 325 °C when the solution became a cloudy yellow. Thermogravimetric analysis confirmed the higher temperature of reaction (Fig. 1, curve B) and again the yellow water-insoluble product was shown to be indium(III) oxide by analysis (found: In 79.0%) and by X-ray powder diffraction.

Hydrated indium(III) sulphate reacted in nitrate melt in two stages (Fig. 1, curve C), the first starting from 120 °C and nearly ceasing at 180 °C, weight loss 6.4 ± 0.2% attributed to dehydration, and the second from 180 °C to 400 °C with a weight loss of 62.8 ± 0.3%, close to that for the reaction

$$\begin{array}{l} In_2(SO_4)_3 + 6NO_3^- \rightarrow In_2O_3 + 3SO_4^{2-} + 6NO_2 + 1\tfrac{1}{2}O_2 \\ (\text{Calc. for loss of } 6N + 15O \text{ per } In_2(SO_4)_3 \text{ } 62.6\%) \end{array} \qquad (2)$$

The yellow solid remaining after washing and drying the quenched reacted melt was identified by analysis (found: In 82.6%). The temperature

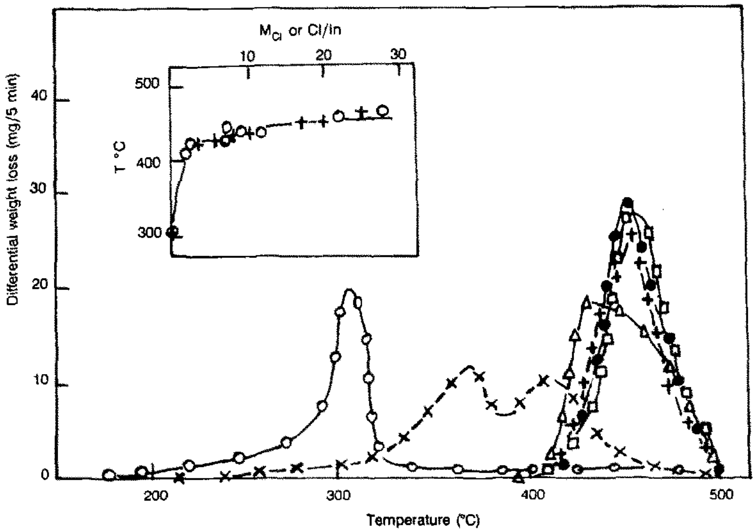

Fig. 2. Thermogravimetric analysis of indium(III) nitrate in lithium nitrate–potassium nitrate eutectic with added potassium chloride: curve A, ○, 0.66 M $In(NO_3)_3$; curve B, ×, 0.49 M $In(NO_3)_3$ + 1.46 M KCl (ratio 1 : 3); curve C, △, 1.12 M $In(NO_3)_3$ + 6.82 M KCl (ratio 1 : 6); curve D, □, 1.12 M $In(NO_3)_3$ + 11.15 M KCl (ratio 1 : 10); curve E, +, 0.49 M In $(NO_3)_3$ + 7.31 M KCl (ratio 1 : 15); curve F, ●, 1.12 M In $(NO_3)_3$ + 22.3 M KCl (ratio 1 : 20). Inset: temperature of maximum rate of weight loss versus chloride concentration (○) and indium:chloride ratio (+).

of maximum rate of weight loss was again higher than that for indium(III) nitrate, as it was also for indium(III) chloride, and both are considered to represent the stabilisation of indium(III) cations towards the Lux–Flood acid–base reaction, by the coordination of ligand anions. This stabilisation was then studied more extensively by reacting indium(III) nitrate with nitrate melt containing different concentrations of ligands, added as the potassium salts.

In the case of potassium chloride (Fig. 2, curves B–F), the temperature of maximum rate of weight loss increased with increase in potassium chloride concentration (Fig. 2, inset), reaching a constant value at 460 °C with chloride: indium ratios of $\geqslant 10$. (Although the ligand : metal ratio is the conventional way of presenting such data, the concentration of a complex is actually proportional to the ligand concentration, or some power thereof. Thus the ligand concentration versus the temperature of maximum rate of weight loss plot is also given in the inset.) In this case the indium chloro complexes are likely to be well known ($InCl_4^-$, with perhaps $InCl_5^{2-}$ or

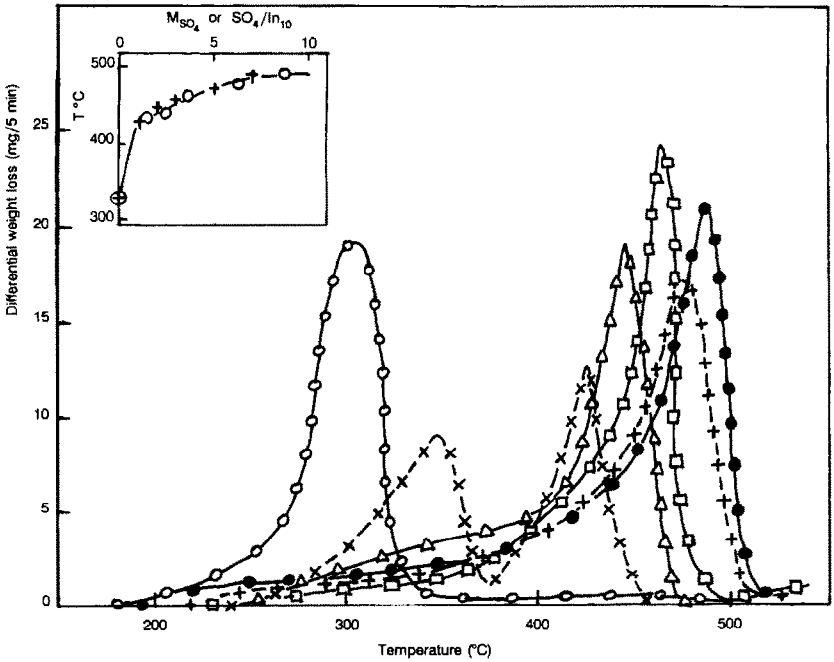

Fig. 3. Thermogravimetric analysis of indium(III) nitrate in lithium nitrate–potassium nitrate eutectic with added potassium sulphate: curve A, o, 0.66 M $In(NO_3)_3$; curve B, ×, 1.24 M $In(NO_3)_3 + 1.25$ M K_2SO_4 (ratio 1 : 1); curve C, △, 1.24 M $In(NO_3)_3 + 2.49$ M K_2SO_4 (ratio 1 : 2); curve D, □, 1.24 M $In(NO_3)_3 + 3.73$ M K_2SO_4 (ratio 1 : 3); curve E, +, 1.24 M $In(NO_3)_3 + 6.22$ M K_2SO_4 (ratio 1 : 5); curve F, ●, 1.24 M $In(NO_3)_3 + 8.73$ M K_2SO_4 (ratio 1 : 7). Inset: temperature of maximum rate of weight loss versus sulphate concentration (o) and indium:sulphate ratio (+).

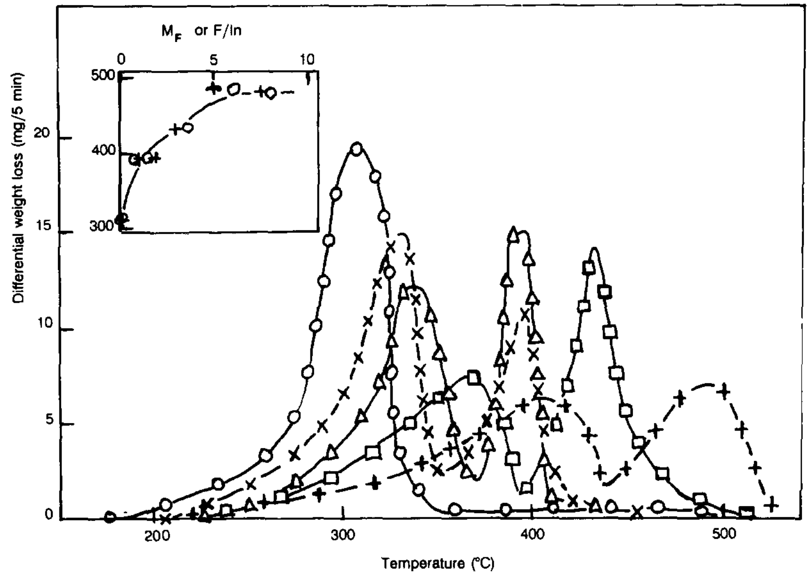

Fig. 4. Thermogravimetric analysis of indium(III) nitrate in lithium nitrate–potassium nitrate eutectic with added potassium fluoride: curve A, ○, 0.66 M $In(NO_3)_3$; curve B, ×, 1.09 M $In(NO_3)_3 + 1.22$ M KF (ratio 1 : 1); curve C, △, 0.42 M $In(NO_3)_3 + 0.85$ M KF (ratio 1 : 2); curve D, □, 1.24 M $In(NO_3)_3 + 3.72$ M KF (ratio 1 : 3); curve E, +, 1.24 M $In(NO_3)_3 + 5.98$ M KF (ratio 1 : 5). Inset: temperature of maximum rate of weight loss versus fluoride concentration (○) and indium:fluoride ratio (+).

$InCl_7^{4-}$) as are found in other media. Similar results were obtained with additions of potassium sulphate (Fig. 3, curves B–F), potassium fluoride (Fig. 4, curves B–E) and potassium iodate (Fig. 5, curves B–G). In each case, indium(III) oxide was the insoluble product and the weight losses were in accord with eqn. (1), being 52.5 ± 1.5, 52.5 ± 1.0, 50.4 ± 0.8 and 54.6 ± 1.3% respectively.

Since only soluble anions can act as ligands and effect this stabilisation, solubility curves for five potassium salts were determined (Fig. 6). Assuming that these solutions were ideal, enthalpies of fusion (L_f) could be calculated from the equation

$$\ln x = \frac{L_f}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) \tag{3}$$

where R is the gas constant, x is the solubility at absolute temperature T and T_m is the melting point of the solute. This gave a value close to that in the literature for potassium chloride (25.42 and 25.62 kJ mol^{-1} respectively) but considerably higher values for the other salts. This was partly due to the experimental inaccuracies, but actual solubilities have been found to be lower than the ideal solubilities for other solutes in molten nitrates [4]. It is evident from Fig. 6, that, except perhaps in the case of potassium iodate, the

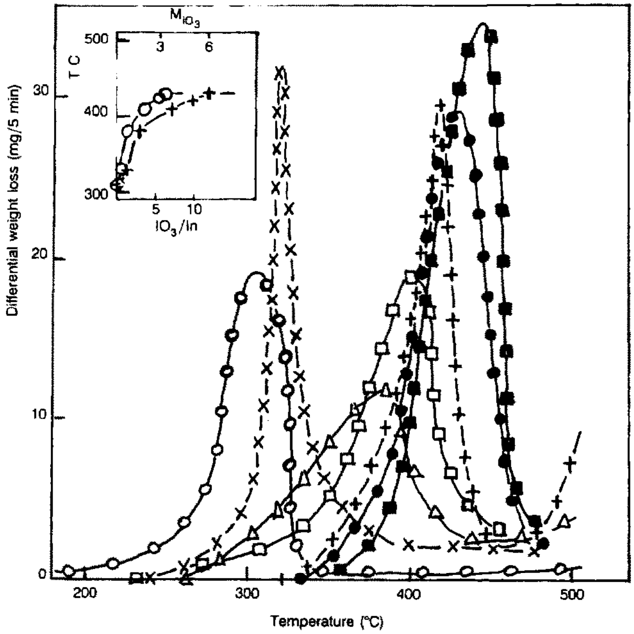

Fig. 5. Thermogravimetric analysis of indium(III) nitrate in lithium nitrate–potassium nitrate eutectic with added potassium iodate: curve A, ○, 0.66 M $In(NO_3)_3$; curve B, ×, 0.25 M $In(NO_3)_3 + 0.26$ M KIO_3 (ratio 1 : 1); curve C, △, 0.24 M $In(NO_3)_3 + 0.72$ M KIO_3 (ratio 1 : 3); curve D, □, 0.25 M $In(NO_3)_3 + 1.28$ M KIO_3 (ratio 1 : 5); curve E, +, 0.26 M In $(NO_3)_3 + 1.83$ M KIO_3 (ratio 1 : 7); curve F, ●, 0.25 M $In(NO_3)_3 + 2.54$ M KIO_3 (ratio 1 : 10); curve G, ■, 0.25 M $In(NO_3)_3 + 3.00$ M KIO_3 (ratio 1 : 12). Inset: Temperature of maximum rate of weight loss versus iodate concentration (○) and indium:iodate ratio (+).

potassium salts of these ligands were substantially less soluble than the maximum ligand concentration effecting the temperature of maximum rate of weight loss, so that in the presence of indium, solubilities are much higher, very largely due to coordination.

In contrast to the above stabilisations, when potassium bromide was present in the melt, indium(III) nitrate reacted at a lower temperature, for example 215 °C rather than 305 °C in pure nitrate (Fig. 7, curve A). This was attributed to the known catalytic effect of bromide on the nitrate–nitrite equilibrium [5]

$$NO_3^- \rightleftharpoons NO_2^- + \tfrac{1}{2}O_2 \qquad (4)$$

and the established much higher basicity of nitrite [6] (~ 10^{10} × self ionisation of nitrate). The considerably higher concentration of oxide ions arising from the nitrite then facilitated the weight loss and formation of indium(III) oxide at significantly lower temperatures than in uncatalysed nitrate melts.

In an analogous fashion, reaction of indium(III) nitrate in nitrate melts containing added potassium nitrite resulted in a maximum rate of weight

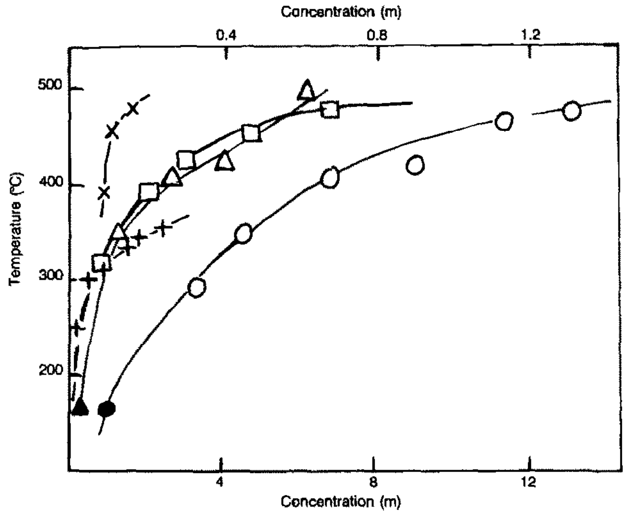

Fig. 6. Solubility of potassium salts in lithium nitrate–potassium nitrate eutectic: curve A, ○, KCl (● value from ref. 4) lower scale; curve B, □, K_2SO_4 upper scale; curve C, ×, KF upper scale; curve D, +, KIO_3 lower scale; curve E, △, KBr (▲ value from ref. 4) lower scale.

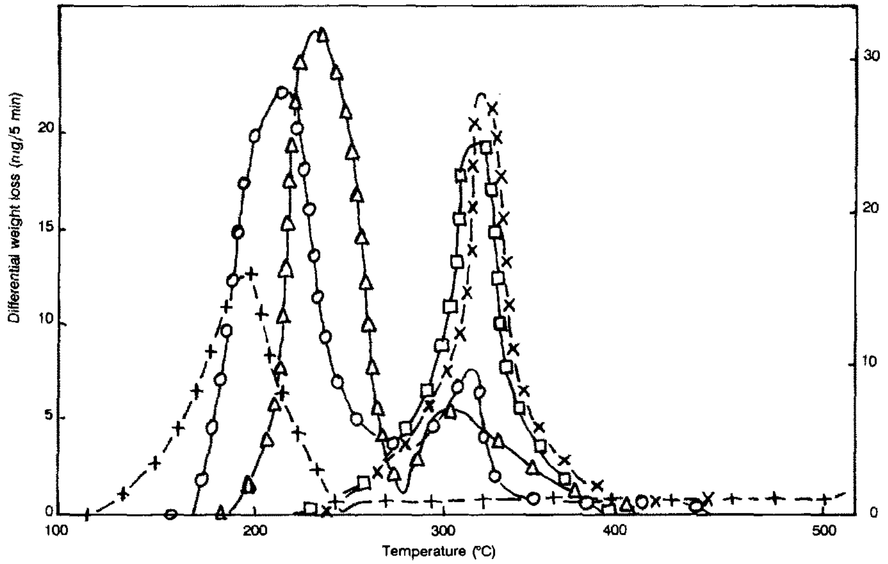

Fig. 7. Thermogravimetric analysis of indium(III) nitrate with added potassium salts: curve A, ○, 1.17 M $In(NO_3)_3 + 1.19$ M KBr (left hand scale); curve B, +, 1.25 M $In(NO_3)_3 + 5.50$ M KNO_2 (left hand scale); curve C, △, 0.34 M $In(NO_3)_3 + 0.69$ M $KClO_3$ (right hand scale); curve D, □, 0.21 M $In(NO_3)_3 + 1.07$ M $KClO_4$ (right hand scale); curve E, ×, 0.23 M $In(NO_3)_3 + 2.33$ M $KClO_4$ (right hand scale).

loss at an even lower temperature (205 ° C, Fig. 7, curve B). The total weight loss was 40.5 ± 0.2% in accordance with the reaction

$$\begin{aligned}&2\mathrm{In(NO_3)_2} + 6\mathrm{NO_2^-} \rightarrow \mathrm{In_2O_3} + 4\mathrm{NO_3^-} + 3\mathrm{NO_2} + 3\mathrm{NO}\\&\left(\text{Calc. for loss of } 3\mathrm{N} + 4\tfrac{1}{2}\mathrm{O} \text{ per } \mathrm{In(NO_3)_3}\ 39.9\%\right)\end{aligned} \tag{5}$$

The reaction of indium(III) nitrate in molten nitrate containing added potassium chlorate also resulted in reaction at a lower temperature than in a pure nitrate, which confirmed an earlier report that chlorate was a stronger base than nitrate [7]. In the present case the temperature of maximum rate of weight loss was 230 ° C (Fig. 7, curve C) and the overall loss was 70.3% suggesting that the postulated chloryl cations

$$2\mathrm{In(NO_3)_2} + 3\mathrm{ClO_3^-} \rightarrow \mathrm{In_2O_3} + 4\mathrm{NO_3^-} + 3\mathrm{ClO_2^+} \tag{6}$$

reacted with the excess chlorate anions

$$\begin{aligned}&\mathrm{ClO_2^+} + \mathrm{ClO_3^-} \rightarrow \mathrm{Cl_2} + 2\tfrac{1}{2}\mathrm{O_2}\\&\left(\text{Calc. for loss of } 1\tfrac{1}{2}\mathrm{Cl_2} + 3\tfrac{3}{4}\mathrm{O_2} \text{ per } \mathrm{In(NO_3)_3}\ 74.4\%\right)\end{aligned} \tag{7}$$

and the remainder with nitrate anions

$$\begin{aligned}&\mathrm{ClO_2^+} + \mathrm{NO_3^-} \rightarrow \tfrac{1}{2}\mathrm{Cl_2} + \mathrm{NO_2} + 1\tfrac{1}{2}\mathrm{O_2}\\&\left(\text{Calc. for loss of } \tfrac{3}{4}\mathrm{Cl_2} + 1\tfrac{1}{2}\mathrm{N} + 3\tfrac{3}{4}\mathrm{O_2} \text{ per } \mathrm{In(NO_3)_3}\ 64.7\%\right)\end{aligned} \tag{8}$$

giving a calculated weight loss for the 2:1 chlorate:indium ratio used of 68.0%.

By contrast potassium perchlorate, which has been reported to be stable in nitrate melts (e.g. at 400 °C in $NaNO_3$) [8], slightly increased the temperature of maximum rate of weight loss from 305 to 320 °C (Fig. 7, curves D and E) which was attributed to some stabilisation of the indium by coordination of perchlorate.

From the extent of stabilisation (i.e. the temperature of maximum rate of weight loss and the ligand concentration) the relative complexing power of the ligands is

$$\mathrm{F^-} > \mathrm{SO_4^{2-}} > \mathrm{Cl^-} > \mathrm{IO_3^-} > \mathrm{ClO_4^-} > \mathrm{NO_3^-}$$

which is comparable with the order in aqueous solutions, except that sulphate is relatively more weakly complexing than chloride in water. This again illustrates the parallel trends in solution properties between water and molten nitrates, largely due to the similarity of coordination by oxygens in both systems.

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