ELSEVIER

Thermochimica Acta 246 (1994) 117–121

thermochimica
acta

# Molten lithium nitrate–potassium nitrate eutectic: the reaction of chromium(III) chloride and nickel(II) chloride

E.I. Eweka, D.H. Kerridge *

*Chemistry Department, The University, Southampton, UK*

Received 21 December 1993; accepted 24 May 1994

## Abstract

In lithium nitrate–potassium nitrate eutectic, nickel(II) chloride was found to undergo a Lux–Flood acid–base reaction from 320°C with a maximum rate at 450°C. Nickel(II) oxide was the solid product and gaseous nitrogen dioxide and oxygen were evolved.

The reaction of chromium(III) chloride in this melt was more complex, the initial reaction from 160°C forming chromium(III) oxide, together with nitrogen dioxide and oxygen, followed at higher temperatures by further reactions to form dichromate at 405°C, and then partially to form chromate from 490°C. The impurity nitrite, present at equilibrium concentration from the thermal decomposition reaction, is considered to be important in determining the reaction temperatures and products, particularly of these latter reactions.

*Keywords:* DTG; Eutectic; Impurity; TGA

## 1. Introduction

The reactions of some compounds of most first-row transition metals have now been examined in lithium nitrate–potassium nitrate eutectic [1], in many cases for oxidation state II or III cations. However two simple cations, chromium(III) and nickel(II), have so far remained unreported. This deficiency is now filled, in both cases the chloride being chosen as the reactant.

---

* Corresponding author.

*SSDI* 0040-6031(94)01913-2

For some time nickel(II) chloride has been known to be slightly soluble in this eutectic (0.16 molal at 160°C [2]) and to be stable at this temperature in chromatography [3] and in ion exchange separation [4] with a solution spectrum interpreted as regular octahedral [5] or tetrahedrally distorted octahedral [6]. However, the acid–base behaviour and reaction temperature have not previously been reported.

In contrast, chromium(III) has been much less studied in lithium nitrate–potassium nitrate, only being reported as stable, in electromigration, at 255°C [7], although in an early paper it was stated to react at 160°C in the ternary lithium nitrate–sodium nitrate–potassium nitrate eutectic [8], which melt would be expected to be of similar, or slightly lower, reactivity than the binary eutectic. Additionally, in sodium nitrate–potassium nitrate, which is definitely less reactive, chromium(III) has been reported to react at 240°C [9] and at 275°C [10], while in pure potassium nitrate at 400°C, chromium(III) chloride was found to form dichromate, nitrogen dioxide and oxygen, although with additional chloride anions present, nitryl chloride and nitrosyl chloride were said to be evolved [11]. Thus the actual reaction temperature of chromium(III) chloride needed to be established in lithium nitrate–potassium nitrate eutectic and its reaction products determined.

## 2. Experimental

### 2.1. Materials

The lithium nitrate–potassium nitrate eutectic was prepared as previously described [2]. Hydrated chromium(III) chloride (RG, Aldrich) was dehydrated by refluxing with thionyl chloride at 70°C for 8 h [12], decanted and then pumped to remove excess thionyl chloride, finally being heated to 200°C under a stream of dry oxygen-free nitrogen. (Found: Cr, 32.50%; Cl, 67.20%. Calc. for $CrCl_3$: Cr, 32.80%; Cl, 67.20%.) Hydrated nickel(II) chloride was dehydrated similarly but at 65°C for 3.5 h. (Found: Ni, 44.70%; Cl, 54.29%. Calc. for $NiCl_2$: Ni, 46.29%; Cl, 54.71%.)

### 2.2. Methods

Reactions were carried out in Pyrex tubes under an air atmosphere, but closed with silica gel guard tubes, and heated in an elelctric furnace controlled with an RS CAL 9000 temperature controller and a step-down transformer.

Thermogravimetric analyses were carried out using a Stanton TR-1 thermobalance with 10 ml silica crucibles and 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 (hatched lines indicate isothermal conditions, when 2°C equals 1 min).

## 3. Results

### *3.1. Reaction of chromium(III) chloride*

The violet solid was insoluble from the melting point to 145°C, when it began to dissolve forming a greenish solution. Brown nitrogen dioxide gas was evolved from 145°C. Thermogravimetric analysis showed that there was a maximum rate of reaction at 160–175°C (Fig. 1, curve A) which slowed down almost completely at 305°C, before a second reaction began at 395°C. During this first reaction the solution was orange and a dark green precipitate was evident from 145°C. This precipitate, after washing and drying, was analysed for chromium(III) oxide. (Found: Cr, 68.75%. Calc. for $Cr_2O_3$, 68.40%.) The weight loss to 395°C was 102.0 ± 1.4% indicating the reaction

$$2CrCl_3 + 6NO_3^- \rightarrow Cr_2O_3 + 6Cl^- + 6NO_2 + 1.5O_2 \qquad (1)$$

(Calc. for loss of 6N + 15O per $2CrCl_3$, 102.5%.)

The colour of the melt indicated that there was a small amount of chromium(VI) formed, probably chromate formed by reaction with the inherent nitrite impurity via the known reaction [13]

$$CrCl_3 + 5NO_2^- \rightarrow CrO_4^- + 3Cl^- + NO_2 + 4NO \qquad (2)$$

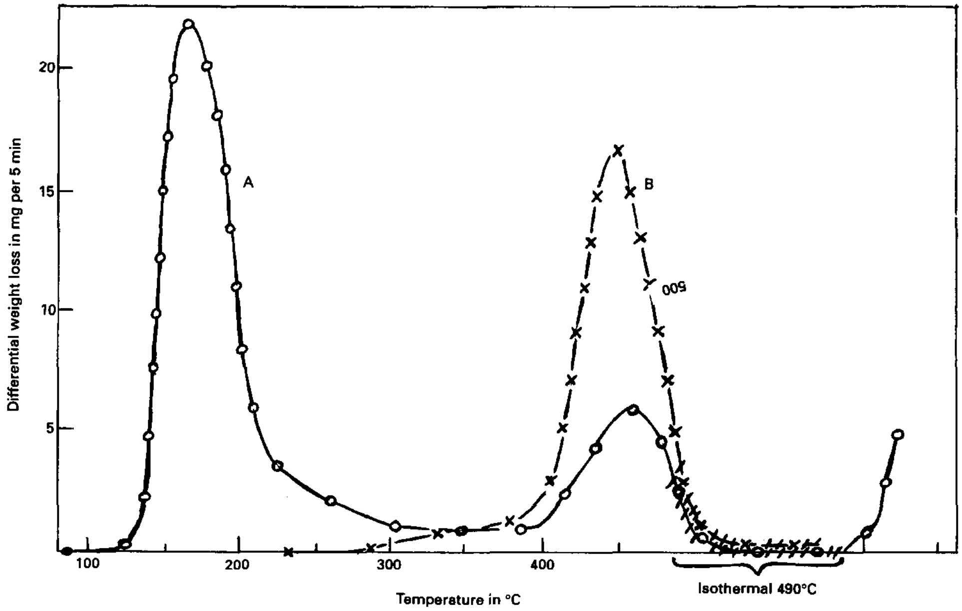

Fig. 1. Thermogravimetric reactions in lithium nitrate–potassium nitrate eutectic. Curve A, 0.47 molal chromium(III) chloride. Curve B, 0.52 molal nickel(II) chloride.

which has a weight loss which is close to that for Eq. (1). (Calc. for loss of 5N + 6O per $CrCl_3$, 104.8%.)

This nitrite impurity arises from the well-known thermal decomposition reaction

$$NO_3^- \rightarrow NO_2^- + 0.5O_2 \qquad (3)$$

which in fact has been shown to be an equilibrium, with a high concentration of nitrite at higher temperatures, e.g. 1.9 molal $NO_2^-$ in $KNO_3$ at 750°C [14]), but with lower nitrite concentrations, e.g. $1.9 \times 10^{-6}$ molal $NO_2^-$ in $NaNO_3/KNO_3$ eutectic at 300°C [15], at lower temperatures.

Thermogravimetry indicated a second reaction at 405°C (Fig. 1, curve A), the gas evolution reaching a maximum rate at 455°C and giving an overall weight loss of 138.7% after 2 h isothermally at 490°C. The melt at this point was orange in colour. A further weight loss commenced on increasing the temperature from 490°C, giving a total weight loss of 146.2 ± 4.6% at 510°C. These second and third weight losses represent further reactions, probably of chromium(III) oxide to dichromate: Eq. (4) predicts the second weight loss closely

$$2CrCl_3 + 11NO_3^- \rightarrow Cr_2O_7^{2-} + 3NO_2^- + 8NO_2 + 2O_2 \qquad (4)$$

(Calc. for loss of 4N + 10O per $CrCl_3$, 136.9%.) The weight loss for formation of chromate (Eq. (5)), however, is rather larger than was found experimentally

$$2CrCl_3 + 11NO_3^- \rightarrow 2CrO_4^{2-} + 6Cl^- + NO_2^- + 10NO_2 + 1.5O_2 \qquad (5)$$

(Calc. for loss of 10N + 23O per $2CrCl_3$, 160.4%.) This indicates only partial formation of chromate. At this point, the melt was observed to be more yellow in colour. The absorption spectrum of the melt held at 490°C showed a maximum at 27 000 $cm^{-1}$, which is between that found for dichromate (26 900 $cm^{-1}$) and that of chromate (27 100 $cm^{-1}$) [16], as would be expected from reactions (1) and (2).

The temperature at which dichromate began reacting was much higher than that previously reported, i.e. 400°C [16], but can be understood in terms of the nitrite impurity present in nitrate melts, being the principal source of oxide ions [16]. Moreover, the rate of nitrite formation in lithium nitrate–potassium nitrate melt increases considerably from 350 to 400°C, for example by ten times between 340 and 390°C [17]. Thus when dichromate is added to fresh nitrate melt, its nitrite content is available for acid–base reaction with formation of chromate, but, after the reaction of chromium(III) chloride, the available nitrite has been removed (Eq. (3)) and the equilibrium nitrite concentration needs to be re-established via the thermal decomposition (Eq. (1)) before further reaction occurs.

This reaction sequence is more complex than expected and illustrates again the probably vital role of nitrite, and of reaction (3), in molten nitrate chemistry. There was no evidence for the evolution of chlorine-containing gaseous species [11], but no additional chloride was added in the above reactions.

### *3.2. Reaction of nickel(II) chloride*

Nickel(II) chloride was slightly soluble in the nitrate melt at 150°C forming a faint yellow solution, which darkened as more solute dissolved with increasing temperature, and was stable (>2 weeks) at 170°C. A slow reaction was visible at 320°C with evolution of brown nitrogen dioxide and formation of a dark grey precipitate. Thermogravimetry showed weight loss began at 280°C (Fig. 1, curve B), with reaction reaching a maximum rate at 450°C and ceasing at 490°C. The total weight loss averaged $86.4 \pm 2.7\%$. The dark grey precipitate, after washing and drying, was analysed. (Found: Ni, 78.10%. Calc. for NiO: Ni, 78.58%.) The precipitate showed the X-ray diffraction lines for nickel(II) oxide: *d* values of the precipitate, 2.09(100), 2.42(100) and 1.48(100); JCPDS Index for NiO, 2.09(100), 2.41(91) and 1.48(57). The reaction was evidently of a Lux–Flood acid–base type

$$NiCl_2 + 2NO_3^- \rightarrow NiO + 0.5O_2 + 2NO_2 + 2Cl^- \tag{6}$$

(Calc. for loss of $2N + 4O$ per $NiCl_2$, 83.3%.) The temperature at which reaction commenced (280°C) was similar to those of other first-row transition metal cations in this eutectic, e.g. $CoCl_2$, 255°C [7], $Cu(NO_3)_2$, 260°C [18], but as would be expected this is lower than the temperature of reaction of nickel(II) chloride in sodium nitrate/potassium nitrate eutectic of 300°C [19], though this difference is minimised because of the high concentration of the reactant in the latter reaction (5.7 molal). The reaction temperature found is also in accord with the earlier evidence involving separation and spectroscopy of nickel solutions [3–6].

## References

[1] D.H. Kerridge, Molten salts as non-aqueous solvents, in J.J. Lagowski (Ed.), The Chemistry of Non-Aqueous Solvents, Vol VB, Academic Press, New York, 1978, Chapter 5.
[2] B.J. Brough and D.H. Kerridge, J. Chem. Eng. Data, 11 (1966) 260.
[3] D.M. Gruen, S. Fried, P. Graf and R.L. McBeth, in Proc. 2nd UN Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 28, p. 112.
[4] G. Alberti, A. Conte and S. Allulli, J. Chromatogr., 18 (1965) 564.
[5] D.M. Gruen, J. Inorg. Nucl. Chem., 4 (1957) 74.
[6] S.V. Volkov and N.I. Buryak, Zh. Neorg. Khim., 17 (1972) 1054.
[7] R.A. Bailey and A. Steger, J. Chromatogr., 11 (1963) 122.
[8] M. Steinberg and N.H. Nachtrieb, J. Am. Chem. Soc., 72 (1950) 3558.
[9] G.G. Bombi and M. Fiorani, Talanta, 12 (1965) 1053.
[10] L.E. Topol, R.A. Osteryoung and J.H. Christie, J. Phys. Chem., 70 (1066) 2857.
[11] M.W.Y. Spink, Diss. Abstr., 26 (1966) 4274.
[12] J.H. Freeman and M.L. Smith, J. Inorg. Nucl. Chem., 7 (1958) 224.
[13] D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 3 (1969) 667.
[14] R.F. Bartholomew, J. Phys. Chem., 70 (1966) 3442.
[15] R.N. Kust and J.D. Burke, Inorg. Nucl. Chem. Lett., 6 (1970) 333.
[16] B.J. Brough, D.H. Kerridge and S.A. Tariq, Inorg. Chim. Acta, 1 (1967) 267.
[17] C.C. Parker, M. Phil. Thesis, University of Southampton, 1979.
[18] H. Frouzanfar and D.H. Kerridge, J. Inorg. Nucl. Chem., 41 (1979) 181.
[19] S.P. Pandey and N.B. Singh, Thermochim. Acta. 67 (1983) 147.