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# Molten sodium nitrite–sodium nitrate–potassium nitrate eutectic: the reactions and spectra of chromium(III) chloride and chromium(VI) compounds

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**Abstract**

In ternary sodium nitrite–sodium nitrate–potassium nitrate eutectic, chromium(III) chloride and potassium dichromate were found to undergo Lux–Flood acid–base reactions to form chromate, which was shown to be soluble and stable. The stoichiometry of the reactions in the presence of the competing basic anions was much more similar to those found in pure nitrite than in pure nitrate melts, but the oxidation of nitrite to nitrate, possibly via nitric oxide and nitrogen dioxide, was shown to be important.

All three reactants had spectra which were also much more similar to those in pure nitrite than in pure nitrate melts.

*Keywords:* Eutectic; Melt; Ternary system

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## 1. Introduction

Molten salt chemistry, particularly that of the simpler melts (i.e. the melts of the alkali metal halides and of the nitrogen oxyanions [1, 2]) has now reached the position that their behaviour and reactions are relatively well understood. However the next stage of complexity, that of melts containing two anions, is in a much less satisfactory state. It is frequently asserted that one anion will be relatively inert whilst the other reacts more or less as in its pure melt. This is probably true in the case of melts containing, for example, chloride and carbonate, but a more intriguing case arises with

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the nitrogen oxyanions, nitrate and nitrite, since both take part, as bases, in Lux–Flood acid–base reactions in their pure melts. What then happens when both the anions are present in roughly equivalent proportions; which anion acts preferentially as the base?

An eutectic which contains both nitrate and nitrite is Heat Transfer Salt (sodium nitrite–sodium nitrate–potassium nitrate, containing 48.9, 6.9 and 44.2 mol%, melting point 142°C), which has very well documented physical properties [3], having been widely used for many years in industry as a coolant and heat transfer medium. A series of studies has therefore been made in this melt of the behaviour of reactants whose reactions are well understood in both pure nitrate and nitrite melts. This paper describes the results for chromium compounds, in both oxidation states III and VI, which also, incidentally, shed some further light on the importance of the impurity nitrite always present in alkali metal nitrate melts from the thermal decomposition equilibrium.

## 2. Experimental

### 2.1. Materials

The ternary sodium nitrite–sodium nitrate–potassium nitrate eutectic was prepared by taking appropriate quantities of the previously dried salts [$NaNO_2$ (BDH Technical) dried at 130°C for 30 h, $NaNO_3$ and $KNO_3$ (both BDH Analar) dried at 180°C for 24 h], mixing, melting and holding at 180°C for 4 h. The melt was then filtered through sintered glass (No. 4 grade) in an oven at 180°C. After solidification and storage in a desiccator, the melt was dehydrated, in batches, by evacuation on a rotary pump, the pressure being reduced gradually, using a needle valve to minimise bumping, then held at $10^{-2}$ Torr for 10 h at 250°C.

Hydrated chromium(III) chloride (RG, Aldrich) was dehydrated by refluxing with thionyl chloride at 70°C for 8 h [4], 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%]. Potassium dichromate and potassium chromate (both BDH Analar) were dried at 120°C for 24 h.

### 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 electric furnace controlled with a 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 $(5\,min)^{-1}$) against temperature (hatched lines indicate isothermal conditions, when 2° equals 1 min).

Electronic absorption spectra were obtained with a Unicam SP-700 spectrophotometer with reversed optics from 4000–13 000 $cm^{-1}$ and with RF-heated cells.

## 3. Results and discussion

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

The violet solid dissolved very slowly at 150°C giving a clear green solution which became more yellowish as the temperature was increased to 175°C when brown nitrogen dioxide was seen to evolve. Thermogravimetry showed a slow reaction from 146°C, which reached a maximum rate at 160°C and ceased at 420°C (Fig. 1, curve A), while a further weight loss began at 435°C. The total weight loss at 420°C was 89.6 ± 1.1%. The reacted solution was bright yellow (absorption maximum

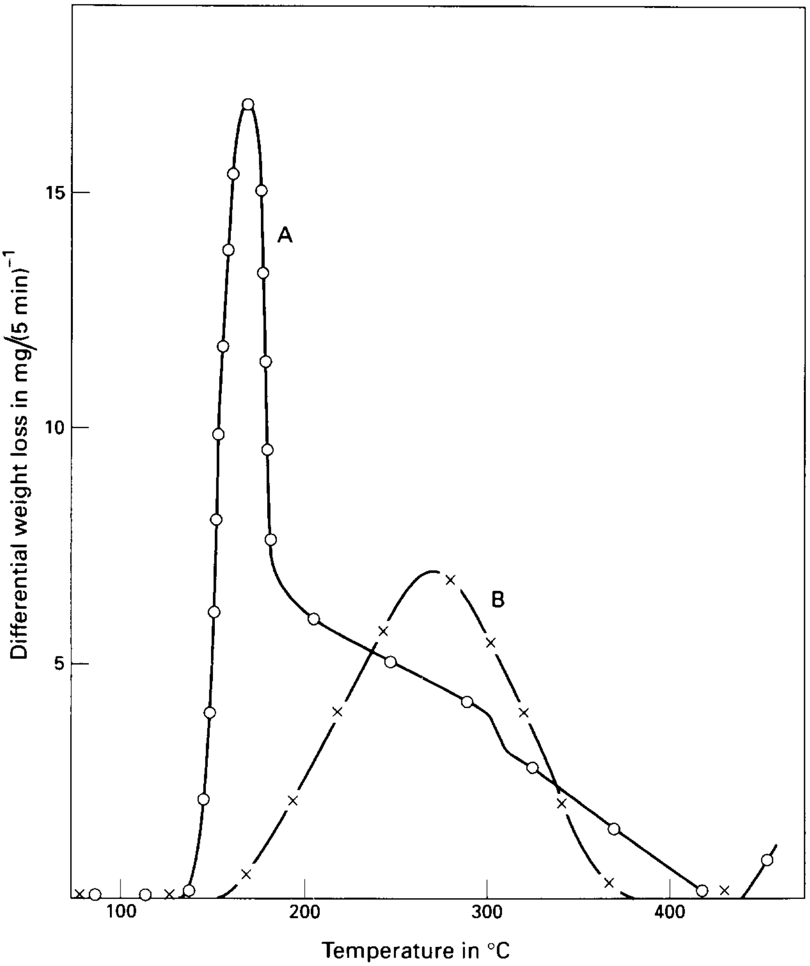

Fig. 1. Thermogravimetric analysis of chromium compounds in sodium nitrite–sodium nitrate–potassium nitrate eutectic. Curve A ○, 0.43 molal chromium(III) chloride. Curve B ×, 0.47 molal potassium dichromate.

24000 cm$^{-1}$) and gave positive tests for chromate(VI). This evidence suggested the reaction

$$CrCl_3 + 6NO_2^- \rightarrow CrO_4^{2-} + NO_3^- + 3Cl^- + 5NO \qquad (1)$$

(Calc for loss of 5N + 5O per $CrCl_3$ 94.7%)

This reaction is much more similar to that found for chromium(III) chloride in a pure nitrite melt (beginning at 200°C, maximum at 275°C, in $NaNO_2$–$KNO_2$ eutectic) [5] than in a pure nitrate melt [6]. However the experimental weight loss was somewhat less than that predicted from Eq. (1). This has been found to be a general feature of reactions in this ternary nitrite–nitrate eutectic. The reason is thought to lie in a further reaction

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

which has been shown to be an equilibrium, the reverse of the well known thermal decomposition reaction, and to occur also at these lower temperatures [7] where the equilibrium position is at very much less nitrite than the composition of this ternary eutectic. This gain of oxygen reduces the size of the weight loss actually observed. No doubt it also occurs in the reaction with the pure nitrite melt [5], but in that case the experimental weight loss was adjusted for the formation of nitrate, whose amount was determined by analysis. No such analysis, and adjustment of weight loss, was possible in the present series of thermograms since the large nitrate concentration inherent in this ternary melt completely concealed a small increase in nitrate concentration due to reaction (2). It should be pointed out that the increase in nitrate concentration in the pure nitrite melt was attributed to a different reaction

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \qquad (3)$$

and it may well be that the presence of nitric oxide, and its ready oxidation by atmospheric oxygen to nitrogen dioxide, together with reaction (3), does facilitate ("catalyse") the attainment of reaction (2). This insight on the importance of reaction (2) for nitrite-containing melts was obscured in the earlier work by the decision to correct for the formation of nitrate. The oxidation of the ternary melt containing no transition metal chloride, with resulting gain in weight by reaction (2), became evident from 600°C using thermogravimetry and continued at least to 700°C, when the increasing rate of weight loss from the well-known thermal decomposition reactions of nitrite and nitrate became dominant.

Although the same overall reaction would result, it is not thought that the chromium(III) chloride reacted with nitrate anions as the source of oxide [8], since in pure sodium nitrate–potassium nitrate eutectic it has been reported to react only above 240°C [9] and at 275°C [10], and because the oxidation of nitrite by oxygen (Eq. 2), and by nitrogen dioxide (Eq. 3), is not sufficiently fast at these temperatures as to ensure that all the gases that would be produced in the Lux–Flood acid–base/redox reaction, i.e.

$$CrCl_3 + 5NO_3^- \rightarrow CrO_4^{2-} + 3Cl^- + 5NO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

would react.

The unreacted clear green solution first obtained with chromium(III) chloride had two absorption bands (at 16500 cm$^{-1}$, 46 M$^{-1}$ cm; and 23 400, 185) which are similar to those found with chromium(III) in sodium nitrite–potassium nitrite eutectic at 230°C [5] and to the solid reflectance spectrum of the hexanitrato complex ($K_3[Cr(NO_3)_6]$) [11], thus suggesting octahedral coordination of the chromium by six nitrito or nitrato ligands (rather than by nitro or chloro ligands), the absorptions being due to $^4T_{2g} \leftarrow {}^4A_{2g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$ transitions respectively. The rather high extinction coefficient of the latter band, compared to the hexachloro chromium(III) complex (18 348, 46) [12] or hexammino complex (28 500, 27) [13], may be due to the presence of quite small amounts of chromate(VI), which absorbs at the same energy.

### 3.2 Reaction of potassium dichromate

Potassium dichromate dissolved slowly in the ternary eutectic at 160°C giving a clear orange solution, which had one absorption band (23 000 cm$^{-1}$, 193 M$^{-1}$ cm$^{-1}$). This energy and intensity are somewhat lower than those found for dichromate in molten nitrate at 160°C (26 900, 2350) [8], but were similar to the band found in pure nitrite melt (23 400, 700 in $NaNO_2/KNO_2$ at 220°C) [5] which was also somewhat asymmetric. In this melt it was considered that the high absorption of nitrite itself at 27 000 cm$^{-1}$ in both the sample and the reference beams caused the major part of the chromate absorption, at a higher energy than 24 000 cm$^{-1}$, to become immeasurable. Despite this, the chromate absorption is considered to be due to the normal ($e \leftarrow t_1$) charge transfer band.

Thermogravimetry (Fig. 1, curve B) showed weight loss began from 195°C reaching a maximum at 250°C and concluding at 375°C. The product was a bright yellow solution giving positive tests for chromate. The overall weight loss was 21.5 ± 0.2 supporting the Lux–Flood acid–base reaction well known in other melts,

$$Cr_2O_7^{2-} + 3NO_2^- \rightarrow 2CrO_4^{2-} + NO_3^- + 2NO \quad (5)$$

(Calc for loss of 2N + 20 per $K_2Cr_2O_7$ 20.4%)

and identical to that reported in sodium nitrite–potassium nitrite binary eutectic [5], once allowance is made for complete reaction of nitrogen dioxide.

### 3.3. Reaction of potassium chromate

Potassium chromate dissolved readily in the ternary eutectic at 220°C to give a bright yellow solution. As expected, no Lux–Flood acid–base reaction was observed on increasing the temperature to 550°C. The absorption spectrum of a 0.015 M solution showed only one absorption maximum (at 24 000 cm$^{-1}$, 838 M$^{-1}$ cm$^{-1}$). Again this band was similar to that found in a pure nitrite melt ($NaNO_2/KNO_2$, 24 000 cm$^{-1}$, 680 M$^{-1}$ cm$^{-1}$ at 230°C), rather than that in a pure nitrate melt [($LiNO_3/KNO_3$, 27 100 cm$^{-1}$, 3620 M$^{-1}$ cm$^{-1}$ at 160°C [8] and $NaNO_3/KNO_3$, 26 900 cm$^{-1}$, 3330 M$^{-1}$ cm$^{-1}$ at 280°C [14])] or in aqueous solution [(26 900 cm$^{-1}$, 4820 M$^{-1}$ cm$^{-1}$ at 20°C [15])]. Again the explanation of this difference is considered to be the strong absorption of nitrite from 23400 cm$^{-1}$, which renders the chromate absorption beyond 24000 cm$^{-1}$ incapable of measurement. The part of this absorption which is measured is still considered to be caused by the customary charge transfer band.

In conclusion it may be said that with each of the reactants in the ternary eutectic, nitrite appears to be the source of the oxide ions, in preference to nitrate. The higher basicity of nitrite has, of course, been known quantitatively since the work of Kust and Burke [7], but the present results show that the preferential reaction of nitrite persists at least down to the almost 1:1 proportion of anions in the ternary eutectic. Such a preferential reaction may well also persist with lower proportions of nitrite and indicate at least part of the reason why so many molten nitrate reactions seem to be dependant on the impurity nitrite concentration, (e.g. of iodate [16], and of chromium(III) chloride [6]), which is always present from the thermal decomposition reaction (reverse of Eq. 2).

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