Thermochimica Acta, 106 (1986) 361–367
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MOLTEN CALCIUM NITRATE TETRAHYDRATE: THE REACTIONS OF SIX CHROMIUM(VI) COMPOUNDS

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(Received 21 February 1986)

ABSTRACT

Calcium nitrate tetrahydrate as a molten salt solvent has a working range of 50 °C before significant evaporation takes place, which can be extended to 90 °C by covering the melt surface with a film of immiscible organic liquid.

Potassium di-, tri- and tetrachromates dissolved but did not react until the temperature range of anhydrous calcium nitrate, when Lux-Flood acid–base reaction occurred forming chromate. Potassium chromate dissolved slightly but was otherwise unreactive. Spectroscopic measurements on melt solutions are reported. Chromium(VI) oxide reacted in the hydrate melt forming nitric acid and probably calcium dichromate, the latter depolymerising in the anhydrous nitrate. Chromyl chloride also hydrolysed in the hydrate melt to hydrogen chloride, nitric acid and calcium chromate.

Above 500 °C the remaining calcium nitrate decomposed to calcium oxide and nitrogen oxides, the reaction possibly being catalysed by chloride. A small amount of chromium(III) was formed when solutions containing chromates were heated to 700 °C.

INTRODUCTION

Hydrate melts are of great interest because of their comparatively low melting points (leading to uses such as solar energy storage [1]) and also because they provide a link between the study of concentrated aqueous solutions and those of the corresponding anhydrous salt melts [2]. Calcium nitrate tetrahydrate has been much used for physical measurements (conductance [3–6], viscosity [4,6,7], density [6,8], thermal conductivity [9], chronopotentiometry [10], polarography [11], and vibrational spectroscopy [6,12,13]) which have been interpreted partly on the basis of water being present only in hydrated cations of large radius (the pseudo-anhydrous molten salt model) and alternatively as evidence of competition of water and nitrate for sites around the calcium ion (the quasi-lattice model). In contrast the behaviour of calcium nitrate as a solvent for chemical reactions has only

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0040-6031/86/$03.50

rarely been reported (e.g. for the nitration of benzene [14], precipitation of silver chloride [15] and association between cadmium and halide ions [16,17]).

Moreover the chemical reactivity of the water molecules of this solvent has not yet been reported despite the considerable potential interest of this question. To open up this area, chromium(VI) compounds (oxyanions, oxide and oxychloride) were chosen as an interesting series for study in this solvent since reaction is known to take place with nitrate anions in anhydrous systems ($LiNO_3/KNO_3$ [18] and $NaNO_3/KNO_3$ eutectics [19]) causing stepwise depolymerisation, and stepwise hydrolysis reactions to occur with water.

EXPERIMENTAL

Calcium nitrate tetrahydrate (BDH AnalaR) was analysed for calcium [found: 16.8%; calc. for $Ca(NO_3)_2 \cdot 4H_2O$: 16.9%] and used without addition of water or drying. Potassium chromate and potassium dichromate (BDH AnalaR) were dried before use (120°C, 24 h) while chromyl chloride and chromium(VI) oxide (BDH reagent grade) were used as received. Potassium trichromate and tetrachromate were prepared by the methods given by Brauer [20] [found: K, 19.1; Cr, 38.8%; calc. for $K_2Cr_3O_{10}$: K, 19.8; Cr, 39.7%, and found: K, 16.2; Cr, 39.7%; calc. for $K_2Cr_4O_{13}$: K, 15.8; Cr, 42.0%].

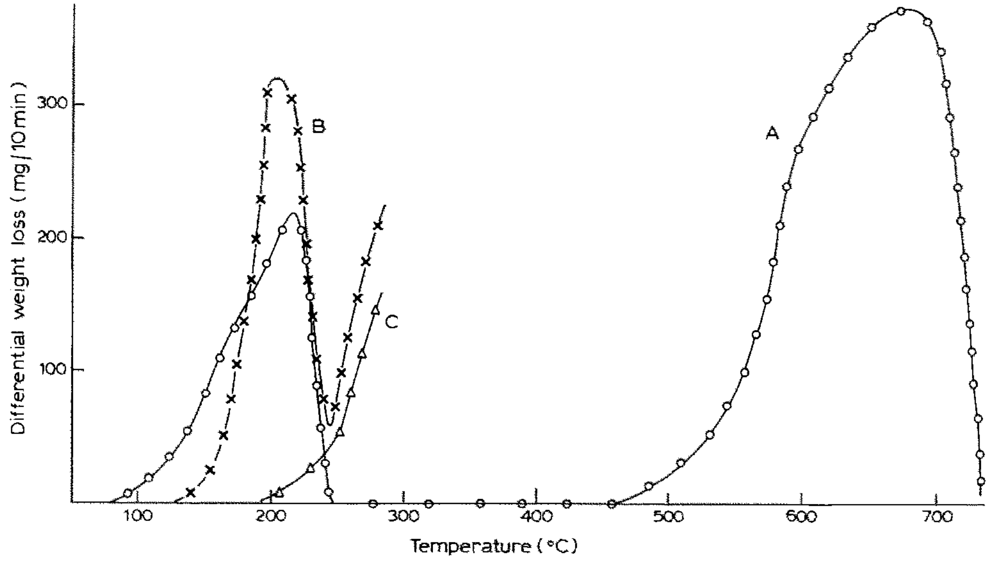

Fig. 1. Thermogravimetric analysis of hydrate melts. (A, ○) 2.0 g $Ca(NO_3)_2 \cdot 4H_2O$, (B, ×) 2.0 g $Ca(NO_3)_2 \cdot 4H_2O$ + 1 ml di-*n*-butylphthalate, (C, △) 1 ml di-*n*-butylphthalate.

Reactions were observed in stoppered tubes heated in an electrical resistance furnace and the electronic spectra of solutions obtained with Shimadzu UV-190, and Unicam SP700 spectrophotometers, the latter adapted for use with a heated cell compartment. Reflectance spectra were obtained with the Unicam SP 735 diffuse reflectance attachment on the SP700. Thermogravimetric analysis was carried out in 10-ml silica crucibles on a Stanton TR-1 thermobalance using a 2°C min^{-1} heating rate. Weight losses averaged over 3–5 determinations are given in mg, or as percentages of weight of original reactant. A film of di-*n*-butylphthalate was only present on the hydrate melt for Fig. 1, curve B. X-ray powder diffraction was carried out using a Phillips (Eindhoven) diffractometer with nickel-filtered CaK_α radiation. Quantitative analysis involved the determination of calcium volumetrically with EDTA, chromium gravimetrically as lead chromate and potassium by flame photometry.

RESULTS AND DISCUSSION

Calcium nitrate tetrahydrate melted at 42.7°C to a colourless mobile liquid with good solvent properties. At higher temperatures water was lost, a

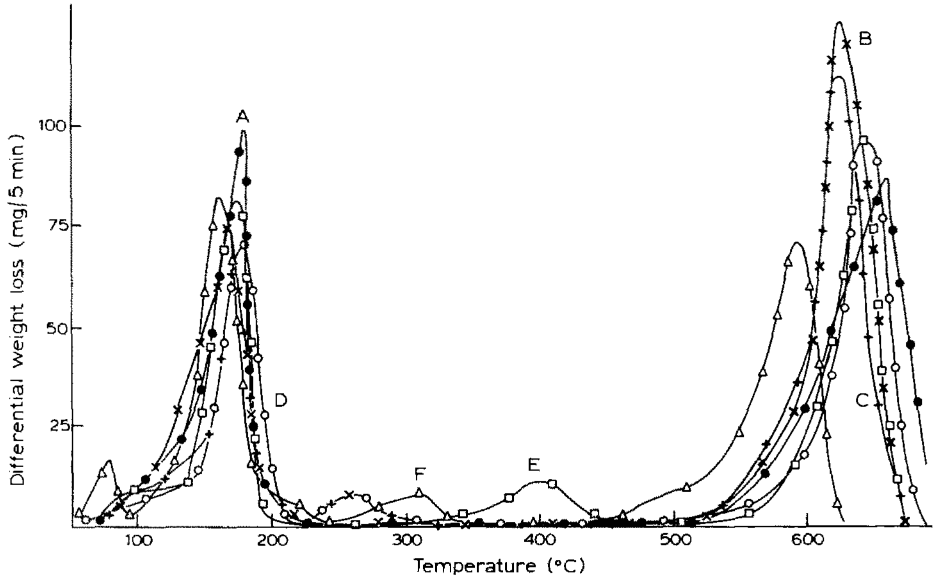

Fig. 2. Thermogravimetric analysis of calcium nitrate tetrahydrate with chromium(VI) salts. (A, ●) 0.33 *m* K_2CrO_4, (B, ×) 0.29 *m* $K_2Cr_2O_7$, (C, +) 0.15 *m* $K_2Cr_3O_{10}$, (D, ○) 0.16 *m* $K_2Cr_4O_{13}$, (E, □) 1.07 *m* CrO_3, (F, △) 1.5 *m* CrO_2Cl_2.

TABLE 1

Absorption maxima (cm^{-1}) and molar extinction coefficients (l mol^{-1} cm^{-1}, in parentheses) for chromium(VI) compounds in various solvents

	K_2CrO_4	$K_2Cr_2O_7$	$K_2Cr_3O_{10}$	$K_2Cr_4O_{13}$	CrO_3
$Ca(NO_3)_2 \cdot 4H_2O$					
50°C	26900(750 [a])	27000(3300)	27400(4400)	27350(5400)	27800(1400)
$LiNO_3/KNO_3$ eutectic [18]					
160°C	27100(3620)	26900(2350)	26700(5550)		
Water					
20°C	26900(4820)	28700(3220)	28500(5020)	28400(4500)	28800(1400)

[a] Minimum value. Some solid undissolved even at 10^{-4} M (possibly $CaCrO_4$?).

process which became significant above 90°C (Fig. 1, curve A). However, if the melt surface was covered with a film of inert, immiscible organic liquid, e.g. di-*n*-butylphthalate, evaporation was considerably reduced and only became apparent above 130°C (Fig. 1, curve B) thus nearly doubling the range of working temperature from 50 to 90°C. Increasing the thickness of the organic surface layer (from 2.5 to 5 mm) had little further effect. Dehydration appeared to be complete by 225–250°C (Fig. 1, curves A and B) with a weight loss of $30.7 \pm 0.1\%$ (calculated for loss of $4H_2O$ per $Ca(NO_3)_2 \cdot 4H_2O = 30.5\%$), the calcium analyses at this point being those expected for the anhydrous nitrate (24.4%). The presence of chromium(VI) compounds as solutes appeared to make little difference to the dehydration reaction (cf. Fig. 2, curves A–D). No evidence was seen for stepwise loss of water [21].

Potassium chromate, though of limited solubility, at 50°C gave a yellow solution but the polychromates dissolved readily to yellow-orange solutions (absorption maxima and molar extinction coefficients being given in Table 1) apparently without reaction. The charge transfer transition found was of very similar energy for each of the chromates as had been previously found in solutions of anhydrous nitrate (e.g. $LiNO_3/KNO_3$ eutectic [18]), and indeed not far from those obtained in water, though in the latter, stepwise hydrolysis of the higher polychromates has taken place ultimately forming dichromate and hydrogen chromate anions (the varying proportions causing the variation in the molar extinction coefficient).

Depolymerisation thus did not take place in the hydrate melt, but thermogravimetric analysis showed that when all water had been evaporated (at > 225°C) the anhydrous calcium nitrate reacted in a single weight loss for each of the three polychromates, all with a closely similar curve (maximum rate of weight loss at 260–270°C, Fig. 2 curves B, C and D) when probably all the depolymerisation took place (i.e. eqns. 1–3). Precise weight losses could not be determined for this second stage because the end of the dehydration continued into it, but certainly more than 98% of the loss expected for eqns. (1)–(3) occurred in this second stage.

$$K_2Cr_2O_7 + 2NO_3^- \rightarrow 2CrO_4^{2-} + 2K^+ + 2NO_2 + \tfrac{1}{2}O_2 \quad (1)$$

$$K_2Cr_3O_{10} + 4NO_3^- \rightarrow 3CrO_4^{2-} + 2K^+ + 4NO_2 + O_2 \quad (2)$$

$$K_2Cr_4O_{13} + 6NO_3^- \rightarrow 4CrO_4^{2-} + 2K^+ + 6NO_2 + 1\tfrac{1}{2}O_2 \quad (3)$$

These reactions were not strictly with solid calcium nitrate since observation showed a highly viscous liquid was present at this stage, whose unusual properties were presumably responsible for the virtually constant reaction temperature, as compared to the variation with polymer length found with anhydrous nitrates [18,19].

Chromium(VI) oxide behaved somewhat differently, since the brown-red solution at 50°C commenced to react above 100°C giving off nitric acid vapour as well as water. The postulated reaction

$$2CrO_3 + Ca(NO_3)_2 + H_2O \rightarrow CaCr_2O_7 + 2HNO_3 \quad (4)$$

received some support from the thermogravimetric results (Fig. 2, curve E) where the second (smaller) weight loss (55.3% of original CrO_3) corresponded well with the reaction

$$CaCr_2O_7 + 2NO_3^- \rightarrow 2CrO_4^{2-} + Ca^{2+} + 2NO_2 + \tfrac{1}{2}O_2 \quad (5)$$

(Calc for loss of $N + 2\tfrac{1}{2}O$ per $CrO_3 = 54\%$)

However, the considerably higher reaction temperature found (350–450°C, maximum at 400°C) suggest calcium dichromate is more stable, as would be expected, but also that where potassium is present (Fig. 2, curves A–D) this is strongly bound to the polychromate anion, which is not anticipated but probably to be attributed to the unusual conditions in the highly viscous liquid.

Chromyl chloride is also reactive at lower temperatures, during the loss of water vapour, as befits the highly hydrolysable molecule. Initially (up to 100°C) some chromyl chloride evaporated from the solution, but from 100 to 200°C hydrogen chloride and nitric acid were evolved as well as water, yellow insoluble calcium chromate was formed and some dissolved to a yellow solution.

$$CrO_2Cl_2 + Ca(NO_3)_2 \cdot 4H_2O \rightarrow CaCrO_4 + 2HCl + 2HNO_3 + 2H_2O \quad (6)$$

Thermogravimetric analysis showed the total weight loss to 360°C to be in agreement with this suggestion (97.7% of weight loss indicated by eqn. (6) plus dehydration of the unreacted calcium nitrate tetrahydrate). The rather elongated second peak found (200–360°C) may indicate a slow loss of hydrogen chloride, stabilised as chlorochromate which is the first hydrolysis product of chromyl chloride, or alternatively and less likely the slow reaction of some intermediate polychromate or even chromium(VI) oxide.

The third peak (500–675°C, maximum weight loss 640 ± 10°C) was very reproducible both with pure melt and with solutions containing oxychromium species, and in every case corresponded well with the weight loss expected for the thermal decompositon of calcium nitrate.

$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + \tfrac{1}{2}O_2 \qquad (7)$$

X-ray powder diffraction on the final solid products did indeed give the lines for calcium oxide, accompanied in the case of Fig. 2, curve A by the lines of potassium chromate indicating the original solute was largely unreacted, in the case of Figure 2, curve B by lines for calcium chromate and for potassium chromate (i.e. as expected for eqn. 1), and in the case of Fig. 2, curve E only by the lines of calcium chromate (i.e. as expected for eqn. 6).

Solution of the greenish-yellow solid residues from heating to > 700 °C in water yielded yellow solutions giving tests for chromate and some green residue which dissolved in concentrated hydrochloric acid to give green solutions on standing with absorptions characteristic of chromium(III) (16400–15400 cm^{-1}). Reflectance spectra of the untreated solid residues also showed maxima at 22800–25400 cm^{-1} indicative of chromium(VI) and a further maximum at 16000 cm^{-1} characteristic of chromium(III). The latter product was presumably due to some high-temperature reduction of the initially formed chromate.

When chromyl chloride was the reactant (Fig. 2, curve F) the third stage (calcium nitrate decomposition) was at a somewhat lower temperature (i.e. starting at 450 °C, with a maximum at 590 °C). The most likely explanation being that some remaining traces of chloride were catalysing the decomposition, as was found with alkali metal nitrates [22,23].

In conclusion, it is clear that the hydrate melt is a good solvent over the rather small temperature range available for experiment (42–130 °C) but is not excessively reactive, since the coordinated water does not appear to cause hydrolysis of the polychromates, but only reacts with the more acidic chromium(VI) oxide and with the highly reactive chromyl chloride. In the hydrate melt environment the nitrate ion is insufficiently basic to cause depolymerisation though it reacts at temperatures above 225 °C, when the calcium nitrate has become anhydrous.

ACKNOWLEDGEMENT

Thanks are expressed to Mr. M.P. Andrews for the preparation and analysis of potassium trichromate and potassium tetrachromate.

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