

## Molten Lithium-Potassium Nitrate Eutectic: the Reactions of Some Compounds of Chromium

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The reactions of six chromium compounds with molten lithium nitrate-potassium nitrate eutectic were studied. The stoichiometry of the oxidation of chromium metal and of chromium(III) oxide, and the stepwise addition of oxide ions to chromium(VI) oxide, trichromate and dichromate to form chromate have been established. The last reaction has been shown to be reversible, dichromate being rapidly formed from chromate by potassium pyrosulphate but very much more slowly by a mixture of nitrogen dioxide and oxygen.

### Introduction

The inorganic chemistry of molten nitrates is still a largely unexplored field. In the case of chromium compounds, the investigations so far reported consist of a kinetic study of dichromate in sodium-potassium nitrate eutectic,<sup>1</sup> some examples of dichromate acting as a Lux-Flood acid<sup>2-8</sup> and of chromium(VI) oxide acting as an acid in potentiometric titrations,<sup>9</sup> the reaction of chromium(III) chloride<sup>10</sup> and a reference to the oxidation of chromium metal.<sup>11</sup> This paper reports a quantitative investigation into the stoichiometry of the reactions of chromium metal, chromium(III) oxide, chromium(VI) oxide, potassium trichromate, potassium dichromate and potassium chromate with lithium-potassium nitrate eutectic.

### Experimental Section

**Materials.** Lithium-potassium nitrate eutectic was prepared as previously reported.<sup>11</sup> B.D.H. electrolytic chromium (99.9%) was crushed and degreased with acetone and ether. Analar  $\text{Cr}_2\text{O}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{K}_2\text{CrO}_4$  were dried at 120° for 6 h.  $\text{K}_2\text{Cr}_3\text{O}_{10}$  was prepared by the method of Harbottle and Maddock<sup>12</sup> (Found :

Cr, 40.1. Calc. for  $\text{K}_2\text{Cr}_3\text{O}_{10}$ . Cr, 39.6%) and  $\text{Cr}_2\text{O}_3$  by heating analar  $\text{K}_2\text{Cr}_2\text{O}_7$  at 700°, leaching and drying at 120° for 6 h. (Found : Cr, 68.8. Calc. for  $\text{Cr}_2\text{O}_3$ , Cr, 68.4%).

**Procedure.** Reactions were carried out in Pyrex tubes with B. 24 joints, closed with silica-gel drying tubes, which fitted snugly into an electric furnace connected to an Ether Transitrol Controller.

**Analysis.** The melts were quenched and dissolved in water. Chromate and dichromate were identified and estimated spectroscopically. Nitrite was detected by the sulphanilic acid- $\alpha$ -naphthylamine test and estimated quantitatively by spectroscopy. (Chromium(III), absorption maximum  $17,400\text{ cm}^{-1}$ , is formed quantitatively from dichromate by nitrite in 2M sulphuric acid). Any remaining chromium was estimated as dichromate. All analyses and measurements are reported as the average of 3-6 measurements.

**Physical Measurements.** Visible and ultraviolet spectroscopy of aqueous solutions was carried out on a Unicam S.P. 800 and of high temperature melt solutions on a Unicam S.P. 700 spectrometer modified for use up to 700°. When chromium species were undergoing depolymerisation (oxide accepting) reactions, extinction coefficients were calculated as  $\text{l. (g. atom Cr)}^{-1} \cdot \text{cm}^{-1}$ , rather than the more customary  $\text{l. mole}^{-1} \cdot \text{cm}^{-1}$ , to avoid arbitrary decisions as to the composition of the chromium containing anion.

Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance with a heating rate of 2° per minute. The weight losses were reported as a percentage by weight of chromium containing starting material. It was found necessary to grind and thoroughly mix the reactant and melt to obtain maximum separation and sharpness of the differential maxima, as otherwise on melting the viscous solutions took some time to achieve homogeneity.

### Results

Chromium metal reacted slowly with lithium-potassium nitrate eutectic at 300° forming a yellow solution which contained considerable quantities of nitrite and liberating brown fumes of nitrogen dioxide. Thermogravimetric analysis indicated an overall weight loss of  $168 \pm 11\%$ . At equilibrium, e.g. after

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20 h. at 300°, the chromium species in the melt consisted entirely of chromate. The absorption maximum was 27100 cm<sup>-1</sup>, ( $\epsilon$  max 3810 ± 40 l. mole<sup>-1</sup> . cm<sup>-1</sup>) and the molar ratio chromate: nitrite was 2: 3.05 ± .03. However initially a considerable proportion of the soluble chromium was present as dichromate ions. The proportion varied with the temperature and amount of chromium metal as well as with the time allowed for reaction but percentages, of soluble chromium present as dichromate, as high as 44% were found. The proportion of nitrite was found to be greater when dichromate was present. For example, after 1/2 hr. of reaction at 350° the percentage of chromium as dichromate was 32% and the molar ratio of chromium (as chromate or dichromate) to nitrite was 2: 3.71.

Chromium(III) oxide was insoluble and unreactive below 250°, but commenced to react at this temperature producing a yellow solution containing chromate and nitrite with evolution of nitrogen dioxide. After pumping off residual nitrogen dioxide the solution absorbed at 27100 cm<sup>-1</sup> ( $\epsilon$  max = 3625 ± 34 l. mole<sup>-1</sup> . cm<sup>-1</sup>), the molar ratio CrO<sub>4</sub><sup>2-</sup>: NO<sub>2</sub><sup>-</sup> was 2: 0.96 ± .01 and the weight loss by thermogravimetry 126 ± 4%.

Chromium(VI) oxide reacted with nitrate eutectic at its melting point (132°) producing orange solutions and copious fumes of nitrogen dioxide. As the temperature was increased more nitrogen dioxide was evolved, the melt ultimately becoming yellow at 500° and giving positive tests for chromate ions. Spectroscopic examination of melt solutions heated to 200° gave an extinction coefficient of 1950 ± 40 l. (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup> (maximum at 26700 cm<sup>-1</sup>). After 24 h. at 260° this fell to 1210 ± 16 l. (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup> and then after heating to 500° for 2 h. rose to 3310 ± 56 l. (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup> (maximum at 27100 cm<sup>-1</sup>). In each case the absorption was measured after the solution had been cooled to 160°. Similar results were obtained from aqueous solutions, that from a melt heated to 200° for 15 min. absorbed at 29000 cm<sup>-1</sup> ( $\epsilon$  max = 1645 ± 40) and that heated at 550° for 2 h. at 27000 cm<sup>-1</sup> ( $\epsilon$  max = 5100 l.) (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup>. Thermogravimetric analysis showed three maxima (Fig. 1).

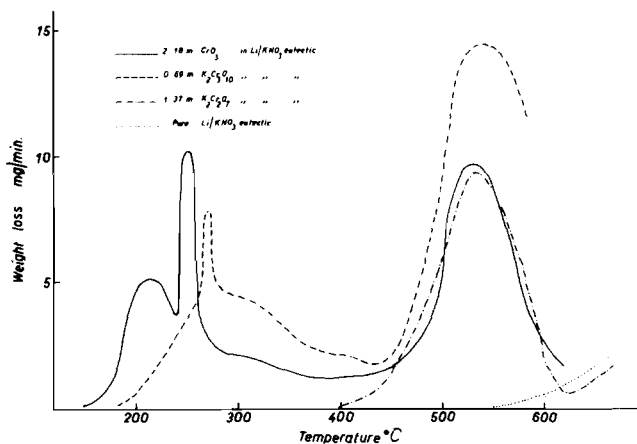


Figure 1. Differential thermogravimetric curves for Cr(VI) compounds. — 2.18 m CrO<sub>3</sub> in Li/KNO<sub>3</sub> eutectic; - - - 0.69 m K<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> in Li/KNO<sub>3</sub> eutectic; - · - · 1.37 m K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in Li/KNO<sub>3</sub> eutectic; ..... pure Li/KNO<sub>3</sub> eutectic.

Although the first two were not well separated the weight loss at 240° was 23 ± 3%. Since the formation of less polymerised chromium species involves the removal of oxide from nitrate ions, the weight loss due to the formation of volatile species, i.e. 2NO<sub>3</sub><sup>-</sup> → O<sup>2-</sup> + 2NO<sub>2</sub>↑ + 1/2O<sub>2</sub>↑, can be calculated from the number of oxide ions removed. In this case the calculated loss for CrO<sub>3</sub> → 1/3K<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> [i.e. loss of 2/3N + 5/3O per Cr] was 36%. The weight loss at 420° was 51 ± 5% (Calc. for CrO<sub>3</sub> → 1/2K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> [i.e. N + 5/2O per Cr] 54%) and at 620° 101 ± 13% (Calc. for CrO<sub>3</sub> → K<sub>2</sub>CrO<sub>4</sub> [i.e. 2N + 5O per Cr] 108%). Isothermal experiments showed a loss of 48% after 10 h. at 225°.

Potassium trichromate dissolved in the melt giving a reddish-orange solution, absorbing at 26700 cm<sup>-1</sup>, ( $\epsilon$  max 5550 ± 34 l. mole<sup>-1</sup> . cm<sup>-1</sup>). Reaction commenced at 200°, nitrogen dioxide being evolved. As the temperature was increased more gases were evolved and the colour lightened. The solution became yellow at 550° and gave positive tests for chromate. After heating for 2 h. at 250° the extinction coefficient fell to 1100 ± 10 l. (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup> (maximum at 26700 cm<sup>-1</sup>) but increased on further heating e.g.  $\epsilon$  max = 1950 ± 10, maximum at 26700 cm<sup>-1</sup>, after 16 h. at 260°, and  $\epsilon$  max = 2300 ± 15, maximum at 27000 cm<sup>-1</sup> after 2 h. at 300°. Thermogravimetric analysis showed two maxima (Fig. 1) which corresponded to a weight loss of 17 ± 3% at 420° (Calc. for K<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> → 3/2K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> [i.e. N + 5/2O] 14%) and 64 ± 3% at 620° (Calc. for K<sub>2</sub>Cr<sub>3</sub>O<sub>10</sub> → 3K<sub>2</sub>CrO<sub>4</sub> [i.e. 4N + 10O] 55%). Isothermal experiments showed a loss of 14% after 2 h. at 250°.

Potassium dichromate dissolved in melt to give orange solutions at 160° absorbed at 26900 cm<sup>-1</sup> ( $\epsilon$  max = 2350 ± 25 l. mole<sup>-1</sup> . cm<sup>-1</sup>). On increasing the temperature a slow gas evolution commenced at 350° which became a brisk evolution of brown fumes of nitrogen dioxide at 400°. During the production of gas the colour of the melt solution slowly changed to yellow with an absorption maximum at 27000 cm<sup>-1</sup> ( $\epsilon$  max = 3840 l. mole<sup>-1</sup> . cm<sup>-1</sup>) and aqueous solutions of the frozen melt gave positive tests for chromate. Thermogravimetric analysis showed one maximum (Fig. 1), the weight loss at 620° being 54 ± 2% (Calc. for K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> → 2K<sub>2</sub>CrO<sub>4</sub> [i.e. 2N + 5O] 37%).

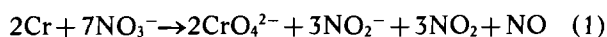
Potassium chromate was soluble in melt at 160° giving a yellow solution absorbing at 27100 cm<sup>-1</sup> ( $\epsilon$  max = 3620 ± 30 l. mole<sup>-1</sup> . cm<sup>-1</sup>). With increasing temperature the solution showed no signs of reaction, either visually or by thermogravimetric analysis, though the colour changed to a more orange yellow. The change in the absorption spectrum was relatively small, the maximum shifting slightly to the red (being 27100 cm<sup>-1</sup> at 200°, 26800 cm<sup>-1</sup> at 400° and 26600 cm<sup>-1</sup> at 500°) but the extinction coefficient remaining constant at 3620 l. mole<sup>-1</sup> . cm<sup>-1</sup>. The most noticeable effect of temperature was a broadening of the band particularly on the long wavelength side, thus giving rise to the greater absorption observed in the visible region.

Addition of potassium pyrosulphate to chromate solutions caused a marked decrease in the extinction coefficient and a shift of the maximum to shorter wavelengths, e.g. a 0.004M chromate solution at 160° after

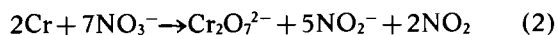
addition of 0.006M pyrosulphate had  $\epsilon_{\max} = 1290 \pm 13$  l. (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup> with the absorption maximum at 28300 cm<sup>-1</sup>. A similar but much slower fall in the extinction coefficient occurred when a mixture of nitrogen dioxide and oxygen (produced by reaction of pyrosulphate and nitrate melt in separate furnace) in a current of nitrogen was passed into a 0.004M chromate solution at 160°. For example, after passing the gases for 21 h. the extinction coefficient fell to  $1110 \pm 57$  l. (g. atom Cr)<sup>-1</sup> . cm<sup>-1</sup> (maximum at 28300 cm<sup>-1</sup>), the pyrosulphate required to produce the gases being equivalent to making the chromate solution 12M in pyrosulphate. Nitrite was found in these melts though none was detected in those in which pyrosulphate was dissolved. Spectroscopic examination of melt solutions of potassium pyrosulphate which were observed to evolve nitrogen dioxide, showed an absorption band of rather variable position with an absorption maximum between 28200 and 28800 cm<sup>-1</sup> ( $\epsilon_{\max} \sim 500$  l. mole<sup>-1</sup> . cm<sup>-1</sup>), which rapidly disappeared on standing (< 3 min.).

## Discussion

The stoichiometry of the reaction of chromium metal with nitrate eutectic suggested by the proportions of reaction products after equilibrium had been attained was



The weight loss calculated for 2N + 7/2O per Cr is 162%, which may be compared to the  $168 \pm 11\%$  found experimentally. However, in view of the initial production of dichromate and more than this molar ratio of nitrite the first reaction may have been

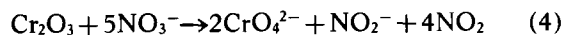


and since the molar ratio of dichromate: additional nitrite (i.e. in excess of that indicated by eqn. 1) was close to 1:2 that this was followed by



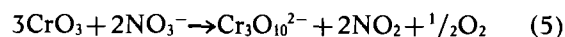
The preferential reaction of dichromate with nitrite in a nitrite/nitrate melt has been observed and is in accord with the more rapid reaction of dichromate in pure nitrite melt (brisk reaction at 250° in sodium-potassium nitrite eutectic).<sup>13</sup>

By contrast the reaction of chromium(III) oxide appeared to take place in only one stage since chromate was the only species detected. This and the ratios of nitrite and gaseous products suggested that the reaction was

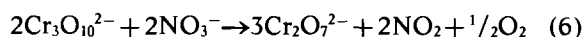


and thus that chromium(III) oxide was not an intermediate in the reaction of chromium metal. Weight loss calculated for 4N + 8O per Cr is 121%, c.f.  $126 \pm 4\%$  found.

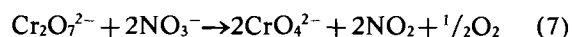
The reactions of the chromium(VI) compounds showed the melt to be acting as a Lux-Flood base (source of oxide ions). The oxide ions appeared to be added stepwise as is illustrated in the differential thermogravimetric curves (Fig. 1). The first maximum on the chromium(VI) oxide curve, maximum rate at 210°, corresponds to the weight loss in the reaction



the second maximum on the chromium(VI) oxide curve and the first on the trichromate curve, maximum rate 250-270°, to the reaction



and the last maximum on the chromium(VI) oxide, trichromate and dichromate curves, maximum rate 530-540°, to the reaction



The close similarity in the temperature and speed of reaction of chromium(VI) species, whether added as such or formed in the melt is well illustrated in Fig. 1. The overlap of reactions, with those of other chromium(VI) species and with the thermal decomposition of the melt, can be seen in Fig. 1 and in the results of the isothermal experiments, and is probably the cause of deviation of the actual weight losses from the calculated values.

The spectroscopic measurements supported the stepwise nature of the addition of oxide ions since extinction coefficients characteristic of trichromate, dichromate and chromate were obtained by heating chromium(VI) oxide solution, those of dichromate and chromate from trichromate and that of chromate from dichromate. There was some evidence from these experiments that trichromate and the dichromate ion formed from it reacted somewhat more rapidly than did the ions formed from chromium(VI) oxide or dichromate added as such.

The position of the absorption band of potassium chromate in nitrate melt was very similar to that in aqueous solution and was very little affected by temperature variation. However the extinction coefficient was rather lower than that in aqueous solution (see Table), but was quite similar to those quoted for potassium nitrate as solvent at 362° with a maximum at 27000 cm<sup>-1</sup> ( $\epsilon_{\max} 3380$  l. mole<sup>-1</sup> . cm<sup>-1</sup>) and lithium-potassium chloride eutectic at 370° (maximum at 27000 cm<sup>-1</sup>,  $\epsilon_{\max} = 3080$ ).<sup>14</sup> Presumably the same charge transfer transition ( $e \leftarrow t_1$ )<sup>15</sup> is responsible for the 27000 cm<sup>-1</sup> band in each solvent. The absorption bands of tri- and dichromate both varied more widely from the aqueous values as did the extinction coefficients. Unfortunately no published values for other fused salt solvents are available for comparison nor have assignments of the charge transfer transitions been made. The absorption bands in solutions produced by reaction

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(15) N. Bailey, Ph. D. Thesis, University of Southampton (1964).

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**Table I.** Absorption maxima and extinction coefficients of chromium(VI) anions

| Solute   | Solvent  |  |                        |  |
|--|--|--|------------------------|--|
|  | LiNO <sub>3</sub> -KNO <sub>3</sub> eutectic<br>160° |  | Aqueous<br>20°         |  |
|  | Absorption<br>Maximum                                | $\epsilon$ max   | Absorption<br>Maximum  | $\epsilon$ max                                 |
| K <sub>2</sub> Cr <sub>3</sub> O <sub>10</sub> | 26700 cm <sup>-1</sup>                               | 5550 ±<br>34 l. mole <sup>-1</sup><br>cm <sup>-1</sup> | 28500 cm <sup>-1</sup> | 5020 l. mole <sup>-1</sup><br>cm <sup>-1</sup> |
| K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>  | 26900  | 2350 ± 25  | 28700                  | 3220 <sup>a</sup>                              |
| K <sub>2</sub> CrO <sub>4</sub>                | 27100  | 3620 ± 30  | 26900                  | 4820 <sup>b</sup>                              |

<sup>a</sup> Aqueous solution contains some hydrogen chromate anion. W. G. Davies and J. E. Prue (*Trans. Farad. Soc.*, 51, 1045 (1955)) give the maximum as 27400 cm<sup>-1</sup> ( $\epsilon$  max = 3800 l. mole<sup>-1</sup>.cm<sup>-1</sup>) for dichromate ion alone. <sup>b</sup> Value from ref. 14.

of other chromium species were observed to be more variable in position than those of solutions made up from pure solvents. This was largely due to the presence of other reaction products and was unavoidable when the chromium anion could itself react further. The chief reaction product, nitrogen dioxide, gave rise to a band of rather variable position, 28200-28800 cm<sup>-1</sup> (the variability probably being due to the production of minute bubbles), with an extinction coefficient large enough to modify the position of the chromium band but without so drastic an alteration of its extinction coef-

ficient as to prevent identification of the chromium species. This effect of nitrogen dioxide was illustrated during the reversal of the dichromate-chromate equilibrium by addition of pyrosulphate. Addition of slightly more than the stoichiometric quantity of pyrosulphate to a chromate solution caused an immediate fall in the extinction coefficient from 3620 to 1290 but the band maximum was shifted to 28300 cm<sup>-1</sup>.

A similar, though much slower, change occurred on passage of the nitrogen dioxide/oxygen mixture through a chromate solution. The relative slowness of this change indicated that nitrogen dioxide was a much less effective Lux-Flood acid than pyrosulphate. Although this slowness may have been due to the less favourable reactive situation of the nitrogen dioxide in the gas bubbles, the results could also suggest that the recent hypothesis of Topol<sup>16</sup> (that nitrogen dioxide is the effective acid species in nitrate melts) may not be applicable to lithium-potassium nitrate eutectic and thus provide support for the earlier hypothesis of Duke<sup>17</sup> that nitryl ions are initially produced when pyrosulphate is added to nitrate melts. Such ions, being strongly acidic, would be expected to readily remove oxide ions from chromate anions.

(16) L. E. Topol, R. A. Osteryoung and J. H. Christie, *J. Phys. Chem.*, 70, 2857 (1966).

(17) F. R. Duke and S. Yamamoto, *J. Amer. Chem. Soc.*, 81, 6587 (1959).