*Contribution from the Department of Chemistry,
The University, Southampton, United Kingdom*

Molten Sodium Nitrite-potassium Nitrite Eutectic: the Reactions of Some Compounds of Chromium

D. H. Kerridge and S. A. Tariq

Received June 24, 1969

The reactions of five chromium compounds with molten sodium-potassium nitrite eutectic were studied. The stoichiometries of the oxidation of chromium(III) chloride and the addition of oxide ions to potassium dichromate, potassium trichromate and chromium(VI) oxide have been established. In each case chromate was the ultimate product. With the last two compounds an intermediate reduction reaction was found to occur, with the formation of chromium(III), either as the solvated ion or in association with chromate. Similar intermediate solutions were observed during the oxidation of chromium(III) chloride.

Introduction

The recent revival of interest in the chemistry of fused salt solvents has not hitherto extended to molten nitrites which have remained among the least studied of the readily available low melting, oxyanion salts of the alkali metals. Published work has been confined to the establishment of phase diagrams,[1,2] a cryoscopic study[3] and some electrochemical investigations on the kinetics of discharged nitrite ions.[4]

However, sodium and potassium nitrite form a eutectic (35 mole % KNO_2) with the conveniently low melting point of 220°, which was reasonably stable up to 500°, though the upper limit of investigation was normally 400° at which temperature attack on pyrex containers became appreciable resulting in opacity and ultimately cracking of the glass. Silica was more resistant but became etched after some days at 400° or above. The eutectic showed considerably greater reactivity than analogous nitrate melts,[5] both in oxidative reactions and when acting as a source of oxide ions. In addition, in some circumstances it also displayed reducing properties. Examples of each of these types of reaction were found during the study of the reactivity and reaction products of five chromium compounds now reported.

Experimental Section

Materials. Analar sodium nitrite (B.D.H.) and reagent grade potassium nitrite (Hopkins and Williams G. P. R.) were dried at 130° for 30 h., cooled, mixed in the eutectic proportions, heated to 250° and filtered through a No. 3 sinter. The melt was dehydrated, in batches, under vacuum (10^{-2} torr) at 230° for 20 h. The batches were combined, frozen and stored. Analysis of the melts indicated an oxide content of $2.1 - 3.6 \times 10^{-2}$ m and $1.8 - 3.5 \times 10^{-2}$ m nitrate. Analar CrO_3, $K_2Cr_2O_7$ and K_2CrO_4 were dried at 120° for 6 h. $K_2Cr_3O_{10}$ was prepared by the method of Harbottle and Maddock.[6] (Found: Cr, 40.1. Calc. for $K_2Cr_3O_{10}$. Cr, 39.6%). Analar $CrCl_3 . 6H_2O$ was dehydrated with thionyl chloride and sublimed in chlorine at 500° (Found: Cr, 32.6; Cl, 67.0. Calc. for $CrCl_3$, Cr, 32.8; Cl, 67.2%).

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 was estimated gravimetrically by precipitation as barium chromate. Nitrate, after decomposing excess nitrite with sulphamic acid, was reduced by iron(II), the excess being titrated against dichromate.[7] Oxide was titrated against standard sulphuric acid. The brown-black chromium(III)/chromium(VI) precipitates were rendered soluble by fusion with lithium-potassium nitrate eutectic and the resulting chromate estimated spectroscopically in aqueous solution. Alternatively, the soluble chromium(VI) was extracted with boiling dilute aqueous sodium hydroxide and estimated spectroscopically as chromate, as was the remaining solid (superficially green chromium(III) oxide) after oxidation to chromate with sodium peroxide. However, this method failed to remove all the chromium(VI) from the solid and resulted in anomalously high chromium(III)/chromium(VI) ratios.

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 modi-

---

(1) P. I. Protsenko and B. S. Medvedev, *Zhur. Neorg. Khim*, *8*, 2737 (1963). P. I. Protsenko and R. P. Shisholina, *Zhur. Neorg. Khim*. *8*, 2741, 2744 (1963). P. I. Protsenko and G. K. Shurdumov, *Zhur. Neorg. Khim*, *9*, 1962 (1964). P. I. Protsenko and N. A. Brykova, *Zhur. Neorg. Khim*, *10*, 1220 (1965).

(2) V. D. Polyakov and S. I. Berul, *Izvest. Sekt. Fiz. Khim. Anal.*, *26*, 164 (1955).

(3) T. R. Kozlowski and R. F. Bartholomew, *J. Electrochem. Soc.*, *114*, 937 (1967).

(4) A. J. Calandra and A. J. Arvia, *Electrochim. Acta*, *11*, 1173 (1966), *12*, 95, 1441 (1967).

(5) B. J. Brough, D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, *1*, 267 (1967).

(6) G. Harbottle and A. G. Maddock, *J. Inorg. Nucl. Chem.*, *5*, 249 (1958).

(7) W. Leithe, *Mikrochim. Acta*, 1960, 762.

fied for use up to 700°. With molten nitrite, measurements were always with 1 mm pathlengths, for both sample and reference, obtained by placing quartz inserts in standard 1 cm Spectrosil cells. The density values of the eutectic employed were those of Polyakov and Berul.[2] When determining the absorption of the pure nitrite against air the cell was filled, then emptied, and the measurement made on the thin film which remained. Diffuse reflectance spectra were obtained with a Unicam S. P. 500 spectrometer fitted with a S. P. 540 attachment.

Infrared spectra of gases were obtained on a Perkin-Elmer Infracord with KBr optics using a 10 cm cell and of solids as Nujol mulls on a Unicam S. P. 200 G.

Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance, normally with a heating rate of 2° per minute, but occasionally with 8° per minute. The weight losses were reported as a percentage by weight of the chromium containing starting material.

Results

Potassium chromate dissolved to give yellow solutions which were stable indefinitely and had an absorption maximum at 24000±60 cm^{-1} with a molar absorptivity of 680±20 l $mole^{-1}$ cm^{-1} (Figure 1 curve A).

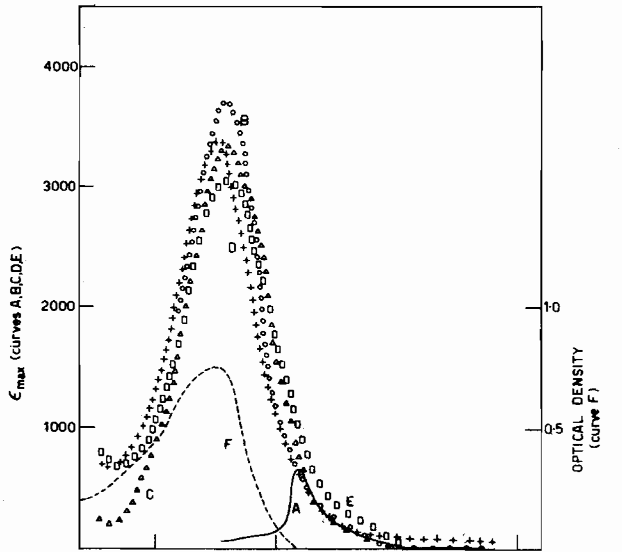

Figure 1. Absorption of chromate ion in nitrite eutectic and other melts. ——— Curve A: K_2CrO_4 in Na/KNO_2 230°[a]; ○○○○ Curve B: K_2CrO_4 in Li/KNO_3 160°[b]; ◃◃◃◃ Curve C: K_2CrO_4 in KNO_3 362°[c]; ++++ Curve D: K_2CrO_4 in KSCN 200°[d]; □□□□ Curve E: K_2CrO_4 in Li/KCl 370°[c]; – – – – Curve F: Pure Na/KNO_2 eutectic 230°[a]. [a] This work; [b] Reference 5; [c] G. P. Smith and C. R. Boston, *Ann. N. Y. Acad. Sci., 79,* 930, 1960; [d] D. H. Kerridge and M. Mosley, *J. Chem. Soc.* (A), 1874, (1967).

Potassium dichromate reacted at, or below, the melting point of the eutectic evolving brown fumes of nitrogen dioxide in dry air, and a mixture of nitrogen dioxide and nitric oxide when reacted under vacuum. The remaining melt was a yellow solution of chromate (ν_{max} 23450 cm^{-1} ε_{max} 700±30 l $mole^{-1}$ cm^{-1}). After solidification the ratio of chromate formed to initial dichromate was found to be 1.97±0.04, and appreciable, though variable, quantities of nitrate were found to be present. Thermogravimetric analysis gave weight losses from 18.3 to 21.1%, the amount varying both with the molarity of dichromate and with the heating rate. However, a correlation was observed between low weight losses and higher nitrate contents. Assuming the nitrate was formed by the reaction,[8]

$$NO_2 + NO_2^- \longrightarrow NO_3^- + NO \qquad (1)$$

the apparent weight losses were corrected (by the addition of 1 O lost per NO_3^- formed) and gave consistent values of 25.1% (Calcd. for loss of 2 N+3 O per $K_2Cr_2O_7$ 25.8%).

Potassium trichromate and chromium(VI) oxide both reacted at or below the melting point to give brown fumes of nitrogen dioxide. If added to the surface of a melt at 230° they produced a brown-black solution which persisted if the concentration of reactant was greater than 0.1 *M*. If more dilute, or if more concentrated on dilution, the dark colour dispersed forming a green-yellow solution, which slowly reacted, producing a yellow melt after 2-4 h. The spectral characteristics of these melts, their aqueous solutions and the reflectance spectra of the solidified melts are given in the Table, together with the ratio of chromate formed to the original reactant.

The weight losses on thermogravimetric analysis varied from 34.1 to 37.9% for trichromate, and 60.5 to 74.7% for chromium(VI) oxide, the variation with chromium(VI) oxide being more marked with a rapid temperature rise, but correcting for the amount of nitrate formed gave a consistent value of 38.5% for trichromate (Calc. for loss of 4N+6O per $K_2Cr_3O_{10}$ 38.5%), and 75.9% for chromium(VI) oxide (Calcd. for loss of 2N and 3O per CrO_3 76.0%).

The brown-black melt gave only a steadily rising absorption over the range 13000-25000 cm^{-1} in reflectance and aqueous spectra. On standing an aqueous solution of the brown-black melts slowly precipitated a brown-black solid containing chromium(III) and chromium(VI) over the course of 3-4 h leaving a clear yellow chromate solution. This precipitate was formed from aqueous solutions of melts with Cr^{VI}/Cr^{III} ratios greater than 9. (In contrast aqueous solutions of the green-yellow melts eventually gave clear yellow chromate solutions and a precipitate of green hydrated chromium(III) oxide. The Cr^{VI}/Cr^{III} ratio in these solutions was found to be much lower varying from 1.8 to 2.8). The brown-black precipitate after drying for 30 h at 110° was shown by the infrared spectrum to contain water, which thermogravimetric analysis indicated was variable in amount but about 20%. The anhydrous precipitate was analysed for chro-

---

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

Table I. Spectral characteristics and ratios of chromium reaction products.

	Final yellow melt			Absorption maxima of intermediate products				
				Green-yellow form			Brown-black form	
Reactant	ν_{max} (cm^{-1})	ε_{max} (l. mole^{-1} cm^{-1})	Ratio of moles of chromate formed to moles of reactant	in melt solution at 230°	in aqueous solution at 20°	solid (reflectance) at 20°)	in aqueous solution at 20°	solid (reflectance at 20°)
$K_2Cr_3O_{10}$	23850	640±30	3.07±0.12	1000-24000 16800 (sh)	>22000 16400	16400	>25000	>25000
CrO_3	23850	710±20	1.00±0.01	21000-24000 16400 (sh)	>22000 16700	16700	>25000	>25000
$CrCl_3$	23500	640±10	0.98±0.06	23400 17000	16400	16400	>25000	>25000

mium (Found: Cr, 57.8. Calcd. for $Cr_2(CrO_4)_3$, Cr, 57.5%) and reacted with lithium-potassium nitrate eutectic, weight loss 106.2% (Calcd. for loss of 10 N + 22O per $Cr_2(CrO_4)_3$ 108.8%.

Chromium(III) chloride commenced to react at 200° although thermogravimetric analysis indicated that the maximum rate occurred at 230-300°. Nitrogen dioxide was evolved and a brown-black solution formed around the crystals. On shaking solutions more dilute than 0.08 *M*, or on dilution of those more concentrated, a green-yellow melt was obtained which on further reaction became yellow, the spectral characteristic of these melts and the ratio of chromate produced are given in the Table I.

Thermogravimetric analysis showed a weight loss which varied from 98.5 to 104.9, however correcting for the nitrate formed in the melt gave a loss of 104.9% (Calcd. for loss of 5 N + 6O per $CrCl_3$ 104.8%).

Discussion

Potassium chromate was found to be stable and soluble in sodium-potassium nitrite eutectic. The large shift in position of the absorption maximum and the reduction in its intensity (the oscillator strength is only about 1/15 of chromate in fused nitrate, thiocyanate or chloride, see Figure 1), is attributed to absorption by nitrite and consequent energy limitation of the spectrometer beyond 25000 cm^{-1}. The asymmetry of the chromate band (Figure 1, curve A) strengthened this suggestion, as did the absence of any new infrared band in the region 4000 to 650 cm^{-1} which might have indicated a chromate-nitrite interaction. However, although the spectrum at frequencies higher than the maximum is not considered to be an attribute of the chromate ion both the position and intensity of this « chromate band » in nitrite were found to be consistent and diagnostic of chromate and were used in the identification of chromium reaction products. The asymmetry of the nitrite band itself (Figure 1, curve F), obtained from a thin film, is probably largely attributable to thinning of the film by drainage whilst the spectrum was obtained, but may also indicate the presence of the 33,300 cm^{-1} band.[9]

Potassium dichromate reacted as expected as a Lux-Flood acid with the formation of chromate,

$$Cr_2O_7^{2-} + 2NO_2^- \longrightarrow 2CrO_4^{2-} + NO_2 + NO \qquad (2)$$

the experimental weight losses agreeing very well with this stoichiometry once allowance was made for the reaction of some nitrogen dioxide to form nitrate (equation 1). The reaction of dichromate with nitrite was considerably more rapid than in lithium-potassium nitrate melts where reaction did not commence until 400°. The possibility that some of the dichromate reacted with the oxide impurity is considered to be a possible explanation of an occasional lower weight loss but measurements with low concentrations of dichromate indicated that the major part reacted with nitrite rather than with oxide ion.

Potassium trichromate and chromium(VI) oxide also reacted ultimately to produce chromate. Analysis and weight losses agreeing well with the overall stoichiometry.

$$Cr_3O_{10}^{2-} + 4NO_2^- \longrightarrow 3CrO_4^{2-} + 2NO_2 + 2NO \qquad (3)$$

and

$$CrO_3 + 2NO_2^- \longrightarrow CrO_4^{2-} + NO_2 + NO \qquad (4)$$

However, it was apparent that in both of the intermediate stages the nitrite had also acted as a reducing agent since chromium(III) was present. It is suggested that in the green-yellow solutions the 16400-16800 cm^{-1} absorption may be best atributed to this ion in an octahedral environment of nitrite oxygen. In the brown-black solutions the colour is attributed to an interaction between chromium(III) and chromium(VI) possibly similar to the brown compound prepared by Chaudhury[10] (from an aqueous solution of $CrCl_3$ and excess Ag_2CrO_4) described as $Cr[Cr(CrO_4)_3] \cdot 3H_2O$. Certainly 0.1 *M* aqueous solutions of chromate and chromium(III) do form brown solutions providing the former is in excess and will give a black-brown precipitate if the ratio is greater than 3. In melt solutions the ratio needed appeared to be higher (>9). However, the solid precipitated from aqueous solutions of these melts also analysed as $Cr_2(CrO_4)_3$ initially associated with approximately $6H_2O$. Oxidation of the anhydrous precipitate in lithium-potassium nitrate eutectic was in accordance with the stoichiometry.

$$Cr_2(CrO_4)_3 + 10NO_3^- \longrightarrow 5CrO_4^{2-} + 10NO_2 + O_2 \qquad (5)$$

---

[9] W. G. Trawick and W. H. Eberhardt, *J. Chem. Phys.*, *22*, 1462 (1954).

[10] P. C. R. Chaudhury, *J. Indian Chem. Soc.*, *16*, 652 (1939).

The nature of the oxidation product of the nitrite formed when chromium(VI) was reduced is somewhat puzzling, since although one could suggest the formation of nitrate

$$2CrO_3+3NO_2^- \longrightarrow 2Cr^{3+}+3NO_3^-+3O^{2-} \qquad (6)$$

this would need to be followed by the preferential reaction of chromium(III) with nitrate, in order to give the overall weight loss and nitrate content found

$$2Cr^{3+}+3NO_3^-+NO_2^-+3O^{2-} \longrightarrow 2CrO_4^{2-}+2NO_2+2NO \qquad (7)$$

However, this seems unlikely both because the nitrate formed in equation 6 would be very dilute and because nitrite has been shown to react preferentially to nitrate. Possibly the intermediate may be some more unusual nitrogen oxyanion which would react preferentially, though no infrared or other evidence was found, no doubt partly due to the low concentration to be expected (maximum $<10^{-3}$ moles). A significant feature of the system was that the equilibrium between chromium(VI) and chromium(III) was very sensitive to chromium concentration, decreasing from $>9:1$ to $<3:1$ with a concentration change from 0.2 to 0.05 *M*.

The reaction of chromium(III) chloride was relatively simple, oxidation taking place forming chromium(VI), ultimately with the stoichiometry,

$$CrCl_3+5NO_2^- \longrightarrow CrO_4^{2-}+3Cl^-+NO_2+4NO \qquad (8)$$

but initially forming a brown-black melt $>0.08\,M$, again attributed to compound formation between the oxidation states, and a green-yellow solution of $<0.08\,M$, again considered to be a simple mixture of chromate and solvated chromium(III) ions.

Acknowledgments. Grateful thanks are expressed to the Science Research Council for a research fellowship to Dr. S. A. Tariq and a grant for spectrometer expenses.