9.87. Found: C, 58.05; H, 3.95; N, 9.50. Here no blue-violet band was eluted by CH_2Cl_2.

The other Ru(LL) complexes were similarly prepared by using the appropriate ligands in the above procedure. Analytical data are as follows. Anal. Calcd for $RuC_{29}H_{26}N_4S_2$ ($Ru(LL)^2$): C, 58.47; H, 4.37; N, 9.41. Found: C, 58.10; H, 4.30; N, 9.52. Anal. Calcd for $RuC_{29}H_{26}N_4S_2$ ($Ru(LL)^3$): C, 58.47; H, 4.37; N, 9.41. Found: C, 58.50; H, 4.40; N, 9.37.

Conversion of $Ru(HL^1)(L^1)Cl$ to RuL^1_2. (a) By Silica Gel. $Ru(HL^1)(L^1)Cl$ (250 mg) was dissolved in dichloromethane (20 mL) and was adsorbed on silica gel (50 g) (BDH, 60–120 mesh). The solvent was removed by evaporation to dryness at room temperature. The dried mass was heated at 323–328 K for 24 h. The red-violet product was then extracted from silica gel with dichloromethane, and the solution was concentrated to ~5 mL. It was subjected to chromatography on a silica gel (BDH, 60–120 mesh) column (30 × 1 cm). A red-violet band was eluted with benzene. On evaporation of the solvent a dark mass deposited. It was crystallized from CH_2Cl_2–CH_3CN (1:5) to yield dark crystals. Yield: 140 mg, (60%).

(b) By Silver(I) Salts. $Ru(HL^1)(L^1)Cl$ (50 mg, 0.08 mmol) was suspended on 20 mL of methanol. To this was added $AgClO_4$ (65 mg, 0.32 mmol), and the mixture was heated to reflux for 30 min. A red-violet solution resulted. After being cooled to room temperature, the solution was filtered through a G4 sintered-glass funnel. The collected solution was evaporated, and the solid mass was subjected to chromatography on a silica gel (BDH, 60–120 mesh) column (15 × 1 cm). A red-violet band eluted with benzene. On evaporation, crystals deposited. These were then dried in vacuum over P_4O_{10}. Yield: 8 mg (17%).

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Registry No. RuL^1_2, 101377-16-6; RuL^2_2, 101377-17-7; RuL^3_2, 101377-18-8; $Ru(LL)^1$, 101402-16-8; $Ru(LL)^2$, 101377-19-9; $Ru(LL)^3$, 101377-20-2; $Ru(HL^1)(L^1)Cl$, 101377-21-3; $Ru(HL^1)(L^1)Br$, 101377-22-4; $Ru(HL^2)(L_2)Cl$, 101377-23-5; $Ru(HL^3)(L^3)Cl$, 101377-24-6; $Ru(HL^3)(L^3)Br$, 101377-25-7; HL^1, 101418-85-3; HL^2, 101418-86-4; HL^3, 101418-87-5; $H_2(LL)^1$, 101418-88-6; $H_2(LL)^2$, 101418-89-7; $H_2(LL)^3$, 101418-90-0; 2-aminothiophenol, 137-07-5; 1,3-dibromopropane, 109-64-8; 1,3-bis((2-aminophenyl)thio)propane, 60435-49-6; nitrosobenzene, 586-96-9; *p*-nitrosotoluene, 623-11-0; *m*-nitrosotoluene, 620-26-8.

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Molten Lithium Sulfate–Sodium Sulfate–Potassium Sulfate Eutectic: Oxidation–Reduction Reactions of Transition-Metal Compounds

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Sulfur dioxide was found to reduce a number of first-row transition-metal compounds in molten ternary sulfate eutectic, the ease of reduction being Cr(VI) > Mn(IV) > Fe(III) > Cu(II). A number of other, probably polymeric, cations (Ti(IV), Nb(V), Mo(VI), Ta(V), W(VI)) were not reduced. Potassium dichromate was unstable, slowly decomposing to chromium(III) oxide, chromate, and oxygen, and was converted to chromate by solutions of sodium carbonate. Chromium metal was little attacked by the ternary eutectic, but copper metal reduced copper(II) to copper(I) cations. Solutions of potassium pyrosulfate decomposed thermally but also oxidized chromium metal (to Cr(III)) and iron(II) (to Fe(III)) and reduced manganese(IV) oxide (to Mn(II)) and chromium(VI) (completely to chromium(III)). Though simple cations (Fe(II), Mn(II)) accelerated the thermal decomposition of pyrosulfate, the more polymeric cations (Ti(IV), Nb(V), Mo(VI), Ta(V), W(VI)) caused considerably less evolution of sulfur trioxide.

Introduction

The systematic study of the chemistry of transition-metal species in molten alkali-metal sulfates is of interest both in its own right as a nonaqueous chemistry and also because of the great practical importance of molten sulfates. Molten sulfates form the reaction films through which the corrosion of high-temperature boilers and heat exchangers occurs and also act as catalysts in the production of sulfuric acid. These catalysts for sulfur dioxide oxidation with air consist of solutions of vanadium, and of other transition metals that act as "promoters", dissolved in molten sulfate and absorbed on kieselguhr.

This paper reports the results of studies of oxidation–reduction reactions of transition-metal compounds, to complement the parallel studies on acidic–basic reactions of these compounds,[1] excluding those of vanadium, which are described elsewhere.[2]

Little has previously been published on oxidation–reduction equilibria in molten sulfates, though there are very brief reports that copper(I) was found to be slowly oxidized to copper(II) (in K_2SO_4–$ZnSO_4$ at 600 °C),[3] possibly by the air atmosphere. However the iron(II)–iron(III) equilibrium (under the same conditions) involved measurable amounts of both oxidation states with a majority of the former.[3] More surprisingly, potassium chromate, under these conditions, was rapidly reduced to chromium(III), which was apparently soluble as spectra were obtained.[3] In contrast, potassium chromate was found to dissolve to give a red melt of reasonable stability in the ternary eutectic (Li_2SO_4 78%, Na_2SO_4 8.5%, K_2SO_4 13.5%) at 550 °C though it was reduced to chromium(III) by magnesium or thallium. These metals also reduced molybdenum(VI) in the same melt, to molybdenum(IV).[4] In addition it has been mentioned that cobalt(III) compounds rapidly decomposed to cobalt(II),[5] while potassium permanganate[3] and potassium tetrachloroplatinate(II)[6] were reported briefly to decompose to unspecified products (all in $K_2SO_4/ZnSO_4$). Many studies, frequently electrochemical, of the corrosion (oxidation) of transition metals have been reported, but in most cases, in pure sulfate melts, insoluble oxides or sulfides resulted.[4,7-11]

Experimental Section

Materials. The ternary eutectic, sodium carbonate, and potassium pyrosulfate were prepared as previously reported[12] as were the transi-

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Table I. Reduction of Copper(II) Sulfate Solution (0.12 *m*) in Ternary Sulfate Eutectic, with Bubbled Sulfur Dioxide (60 mL/min)

temp, °C	time of SO_2 passage, h	% reduction	
		from Cu produced	from Cu(II) titration
580	20	39.1	37.7
610	5	17.3	17.4
610	20	59.7	61.2

Table II. X-ray Powder Diffraction Lines of Solidified Copper(II) Sulfate in Ternary Sulfate Eutectic after 20-h Reduction with Bubbling Sulfur Dioxide

"*d*" spacings and intensities, Å		assignments of obsd lines
reduced $CuSO_4$ soln	Cu_2SO_4[a]	
3.17 (s)[b]	3.16 (100)	$Li_2SO_4 + Cu_2SO_4$
2.73 (m)	2.69 (23)	$Na_2SO_4 + Cu_2SO_4$
2.42 (m)	2.43 (11)	$K_2SO_4 + CuSO_4 + Cu_2SO_4$
2.31 (w)	2.33 (11)	Cu_2SO_4
2.16 (w)	2.16 (11)	Cu_2SO_4
2.11 (w)	2.12 (11)	$CuSO_4 + Cu_2SO_4$
1.79 (w)	1.81 (16)	$CuSO_4 + Cu_2SO_4$

[a] From ref 16. [b] s = strong; m = medium; w = weak.

tion-metal sulfates and oxides.[1] Chromium (BDH electrolytic, 99.9%) was crushed to a fine powder, degreased, and dried at 60 °C. Copper powder (AR, >>99.9%) was used as received. Potassium chromate and dichromate (AR) were dried at 110 °C. Sulfur dioxide, nitrogen, air, and sulfur trioxide were obtained and purified as previously described.[12]

Procedure. The reactions were carried out as previously described.[12] Products were detected qualitatively and estimated quantitatively by conventional methods. Copper(I) in cooled melts disproportionated on solution in water to brown insoluble copper particles and soluble copper(II). The metal was weighed after filtration, washing, and drying and the blue aqueous solution titrated by using EDTA with Fast Sulfon Black F as indicator. Sulfur trioxide was absorbed by using a modification of the methods of Gillham[13] and Flint,[14] employing a water-propan-2-ol solution to avoid oxidation of sulfur dioxide when boiling to concentrate. The sulfuric acid resulting was estimated by addition of excess barium perchlorate and titration of the excess with a standard sodium sulfate solution, using nitrosulfonazo III absorption indicator in water-propan-2-ol.[15] Solid products were also identified by X-ray powder diffraction as earlier described.[12]

Thermogravimetric analysis was carried out on a Stanton TR-1 thermobalance using a 10-mL silica crucible for low-temperature reaction, which was substituted by a 10-mL pure gold crucible (Johnson-Matthey Grade 2) for reactions significantly above 500 °C, to avoid the possibility of silica reacting with basic species in the melt. A water-cooled baffle-plate attachment (Stanton-Redcroft No. 8726) was fitted so that thermogravimetry could also be carried out in poisonous/corrosive atmospheres containing sulfur dioxide and sulfur trioxide. Weight changes, the average of three or more determinations, are reported as grams per mole of initial reactant where this is helpful in interpretation of reaction stoichiometries.

Results and Discussion

Copper. When sulfur dioxide was bubbled through the green solution of copper(II) sulfate dissolved in ternary sulfate eutectic at 580 °C, white fumes of sulfur trioxide were evolved immediately, and the solution slowly became paler. After 5 h, the solution was pale yellow and gave positive tests for copper(I) cations. No other gaseous or dissolved sulfur species were detected, nor was any copper metal precipitated. The extent of reduction of 0.12 *m* solutions (Table I) increased with time and with temperature but was far from complete below the decomposition temperature (which begins at 630 °C in molten sulfate solution[1]). However, solidified solutions after 20-h treatment showed the X-ray powder diffraction lines of copper(I) sulfate, although in some cases these overlapped with lines due to alkali-metal sulfates or the unreduced copper(II) sulfate still present (Table II).

Table III. Reduction of Iron(III) Sulfate Dissolved in Ternary Sulfate Eutectic by Bubbling Sulfur Dioxide/Nitrogen Mixtures

$[Fe_2(SO_4)_3]$, M	temp, °C	gas atmosphere, vol %		time of passage, h	% redn
		SO_2	N_2		
0.12	550	12	88	3	46.6
0.12	550	30	70	2	55.7
0.12	550	100	0	5	>95
0.05	580	25	75	2	95 ± 2

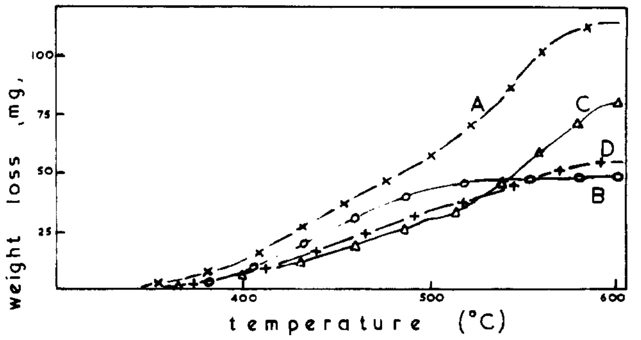

Figure 1. Thermogravimetric analysis with potassium pyrosulfate in ternary sulfate eutectic (3 g) under nitrogen: A (×), 1 mmol of $FeSO_4$, 1.5 mmol of $K_2S_2O_7$; B (○), 1 mmol of $FeSO_4$, 1.0 mmol of $K_2S_2O_7$; C (△), 1 mmol of $K_2S_2O_7$; D (+), 1 mmol of MnO_2, 1.5 mmol of $K_2S_2O_7$.

These results clearly support the reduction

$$2CuSO_4 + SO_2 \rightarrow Cu_2SO_4 + 2SO_3 \qquad (1)$$

and do not suggest that this took place via the production and reaction of sulfite or of its disproportionation products (i.e. sulfide or sulfur).[12] Thermogravimetric analysis did not provide more quantitative information due to an even less complete reaction, caused by the need to pass the gas stream over rather than through the melt and to work with a gas dilute in sulfur dioxide. Under these conditions, the low solubility of sulfur dioxide (a concentration of 0.0007 ± 0.0003 *m* dissolved in molten sulfate eutectic was found in equilibrium with 6% sulfur dioxide/94% air at 580 °C) resulted in even less reduction of copper(II). (For example, 2 mmol of $CuSO_4$ in 3 g of eutectic, under 12% SO_2/88% N_2, gave a weight loss of only 12 mg after $3^1/_2$ h at 630 °C, as compared to 160 mg if reaction had been completed according to eq 1.)

However, addition of copper metal as powder to copper(II) solutions in molten sulfate caused the originally pale green color to fade, becoming a very pale yellow after 4 h at 580 °C when the amount of insoluble copper powder was visibly diminished. Qualitative tests showed the presence of copper(I) in the melt and that the reaction

$$CuSO_4 + Cu \rightarrow Cu_2SO_4 \qquad (2)$$

had occurred. This again illustrated the enhanced stability of copper(I) in the sulfate melt as compared to that in aqueous solution, for the reverse reaction of eq 2 was used as a quantitative method for estimating copper(I) (see Table I, column 3). Similarly, copper(I) has long been known to be more stable than copper(II) in molten chlorides,[17] and indeed compounds of copper(II) have frequently been employed as oxidants.

Iron. Iron(III) sulfate was also soluble in molten sulfate eutectic at 550 °C and also gave sulfur trioxide immediately after sulfur dioxide was passed through the solution, when iron(II) was detected in the quenched melts. The extent of reduction (Table III) was much greater than was found with copper(II) (Table I) in parallel with the much greater ease of reduction found in aqueous chemistry. However under the less favorable conditions imposed

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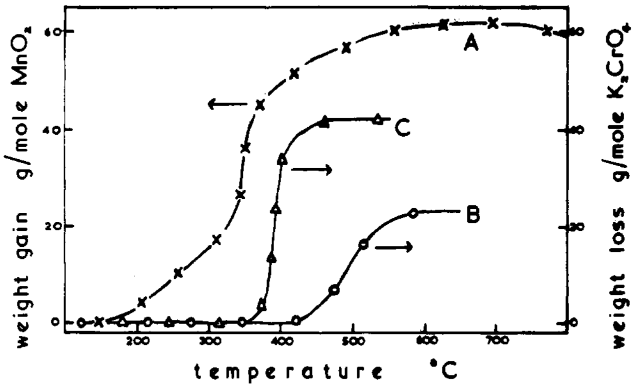

Figure 2. Thermogravimetric analysis in ternary sulfate eutectic (3 g): A (×), 1 mmol of MnO_2 under SO_2 (12%)/N_2 (88%); B (○), 1 mmol of K_2CrO_7 in air; C (△), 1 mmol of $K_2Cr_2O_7$, 1 mmol of Na_2CO_3 in air.

by thermogravimetry, considerably less reduction was again found. For example, 0.33 mmol of $Fe_2(SO_4)_3$ in 2 g of eutectic under 12% SO_2/88% N_2 gave a weight loss of 4 mg after $1^1/_2$ h at 550 °C. Titration showed 9% of iron(II), which corresponded to a 5.5-mg weight loss calculated from the equation

$$Fe_2(SO_4)_3 + SO_2 \rightarrow 2FeSO_4 + 2SO_3 \quad \text{(calcd weight loss 160 g/mol of } Fe_2(SO_4)_3\text{)} \tag{3}$$

The greater ease of reduction of iron(III) was paralleled by the reversal of eq 3 when iron(II) sulfate was heated with potassium pyrosulfate dissolved in sulfate eutectic. With a 1:2 excess of pyrosulfate (Figure 1, curve A) the weight loss of 113 g/mol of $FeSO_4$ corresponded closely to that expected for the reactions

$$2FeSO_4 + 2K_2S_2O_7 \rightarrow Fe_2(SO_4)_3 + 2K_2SO_4 + SO_2 \quad \text{(calcd weight loss 32 g/mol of } FeSO_4\text{)} \tag{4}$$

and

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_3 \quad \text{(calcd weight loss 80 g/mol of } K_2S_2O_7\text{)} \tag{5}$$

However with a 1:1 ratio the weight loss was 48 g/mol of $FeSO_4$ (Figure 1, curve B), indicating that probably before reaction 4 occurred, a third of the pyrosulfate had decomposed via reaction 5. The latter reaction occurred slightly faster in the presence of iron(II)/iron(III), probably because of their higher Lux–Flood acidities (cf. Figure 1, curve C). Similar effects were found with other transition-metal cations.

Manganese. Manganese dioxide, which was insoluble in ternary sulfate eutectic at 580 °C, dissolved when potassium pyrosulfate was present by a reaction

$$MnO_2 + K_2S_2O_7 \rightarrow MnSO_4 + K_2SO_4 + {}^1/_2O_2 \quad \text{(calcd weight loss 16 g/mol of } MnO_2\text{)} \tag{6}$$

analogous to those found in the aqueous system with hot mineral acids and in molten nitrates containing Lux–Flood acids.[18] Again the excess pyrosulfate decomposed slightly faster (Figure 1, curve D) than in the absence of manganese (cf. Figure 1, curve C). The weight loss of 56 mg (from 1 mmol of MnO_2 and 1.5 mmol of $K_2S_2O_7$) agreed very well with reactions 6 and 5. However in contrast to the oxidation of iron (eq 4), eq 6 represents reduction of manganese.

Manganese dioxide in ternary sulfate eutectic at 580 °C was also readily reduced by passage of sulfur dioxide, no doubt again due to the high stability of manganese(II) cations, which were detected in the solidified melt. Thermogravimetry showed weight gain (absorption of SO_2) to begin in the solid state at 160 °C (Figure 2, curve A) but to accelerate markedly at 340 °C, when partial melting began. The overall gain (of 61 g/mol of MnO_2) at 600 °C indicated nearly complete reduction, i.e.

$$MnO_2 + SO_2 \rightarrow MnSO_4 \quad \text{(calcd weight gain 64 g/mol of } MnO_2\text{)} \tag{7}$$

The slow loss from 730 °C, when a small amount of brown solid (Mn_3O_4) was deposited, is in accord with the decomposition[1]

$$3MnSO_4 \rightarrow Mn_3O_4 + SO_2 + SO_3 \tag{8}$$

Chromium. Potassium chromate(VI) dissolved in ternary sulfate eutectic at 580 °C to an orange-red solution (K_2CrO_4 alone also becomes more red and more intensely colored with increasing temperature, as the ultraviolet absorption band broadens with a greater overlap of the visible). No visible precipitate or gas was observed, and thermogravimetry indicated no weight loss up to 900 °C, subsequent analysis showing less than 1% reduction had occurred. In contrast, potassium dichromate was unstable; a red solution formed at 580 °C together with a green precipitate (Cr_2O_3 by X-ray powder diffraction, of weight equivalent to 50 ± 2% of the original chromium added) and a colorless gas. Thermogravimetry (Figure 2, curve B) showed the loss to begin from 420 °C and to reach 23 ± 1 g/mol of $K_2Cr_2O_7$ at equilibrium (600 °C). Again half the chromium had been reduced to chromium(III) oxide, the remainder being present as chromium(VI), in agreement with the equation

$$2K_2Cr_2O_7 \rightarrow 2K_2CrO_4 + Cr_2O_3 + {}^3/_2O_2 \quad \text{(calcd weight loss 24 g/mol of } K_2Cr_2O_7\text{)} \tag{9}$$

which is the stoichiometry reported by Flood and Muan[19] for decomposition of pure potassium dichromate, though their measured equilibrium constant suggests that reaction was more complete in molten sulfate solution. However, the extent of decomposition and the temperature at which it is detectable have been variously reported, Hempel and Schubert[20] quoting 500 °C for the latter, while Duval[21] gave 625–650 °C and suggested 1% decomposition at 700 °C (reached at well below 400 °C according to Flood and Muan). Change of cation may well produce large effects (e.g. Stanley[22] gave 400 °C as the decomposition temperature of sodium dichromate), which could be very significant in melt solution. Moreover, when one considers the overall stoichiometry (eq 9), other reaction schemes are also possible. For example, Hassanien and Kordes,[23] who used potassium dichromate as a cryoscopic medium (and incidentally who found no significant decomposition at its melting point, 400 °C), reported that the freezing point depressions with sodium sulfate or potassium sulfate were consistent with the formation of chromate and a novel anion

$$Cr_2O_7^{2-} + SO_4^{2-} \rightarrow CrO_4^{2-} + CrSO_7^{2-} \tag{10}$$

the latter forming the associated anion $LiCrSO_7^-$ when lithium cations were present. If these novel anions were unstable in sulfate melts at 420 °C and above, e.g.

$$2CrSO_7^{2-} \rightarrow 2SO_4^{2-} + Cr_2O_3 + {}^3/_2O_2 \tag{11}$$

then the ready decomposition found (cf. eq 9) would be explained.

Thermogravimetry of equimolar potassium dichromate/sodium carbonate in the ternary eutectic showed weight loss to occur rapidly above 350 °C (Figure 2, curve C, weight loss to equilibrium (470 °C) 42 g/mol of $K_2Cr_2O_7$) in accordance with the acid–base reaction

$$K_2Cr_2O_7 + Na_2CO_3 \rightarrow 2NaKCrO_4 + CO_2 \quad \text{(calcd weight loss 44 g/mol of } K_2Cr_2O_7\text{)} \tag{12}$$

though a small amount of chromium(III) oxide (2 ± 1% of chromium initially added) in the quenched melt indicated some

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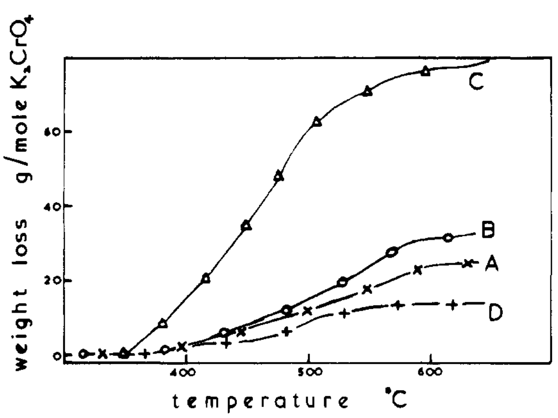

Figure 3. Thermogravimetric analysis of potassium chromate and potassium pyrosulfate in ternary sulfate eutectic (3 g): A (×), 1 mmol of K_2CrO_4, 1 mmol of $K_2S_2O_7$ in nitrogen; B (○), 1 mmol of K_2CrO_4, 2 mmol of $K_2S_2O_7$ in nitrogen; C (△), 1 mmol of K_2CrO_4, 3 mmol of $K_2S_2O_7$ in nitrogen; D (+), 2 mmol of K_2CrO_4, 1 mmol of $K_2S_2O_7$ in air.

decomposition as eq 9. However with the addition of the Lux–Flood acid potassium pyrosulfate to potassium dichromate solutions, all the chromium was reduced to chromium(III) oxide, or to violet chromium(III) solutions if the pyrosulfate was in excess.

Similar reactions occurred when potassium pyrosulfate was added to potassium chromate dissolved in ternary eutectic. An equimolar ratio of potassium chromate and potassium pyrosulfate reacted thermogravimetrically (Figure 3, curve A, weight loss to equilibrium 24 g/mol of K_2CrO_4) in accordance with the overall equation

$$2K_2CrO_4 + 2K_2S_2O_7 \rightarrow 4K_2SO_4 + Cr_2O_3 + {}^3/_2O_2 \quad \text{(calcd weight loss 24 g/mol of } K_2CrO_4\text{)} \qquad (13)$$

since the cooled melt contained no pyrosulfate and chromium only as chromium(III) oxide. However the mechanism may well be via the formation of dichromate

$$2K_2CrO_4 + K_2S_2O_7 \rightarrow 2K_2SO_4 + K_2Cr_2O_7 \qquad (14)$$

and its subsequent reaction (eq 9). Certainly with excess pyrosulfate some of the chromium(III) oxide dissolved

$$Cr_2O_3 + 3K_2S_2O_7 \rightarrow Cr_2(SO_4)_3 + 3K_2SO_4 \qquad (15)$$

but this reaction was not quantitative, because with a 1:2 mole ratio (Figure 3, curve B) the weight loss was 31 g/mol of K_2CrO_4 whereas eq 13 and 15 would suggest a loss of only 24 g/mol of K_2CrO_4. Thus some pyrosulfate probably decomposed via eq 5, causing the higher loss observed. Similarly with a 1:3 mole ratio (i.e. 1 mmol of K_2CrO_4, 3 mmol of $K_2S_2O_7$) when 1.5 mmol of pyrosulfate might have been expected to react as eq 15, and 0.5 mmol as eq 5, giving an overlal loss of 64 g/mol of K_2CrO_4, in fact (Figure 3, curve C) a loss of 77 g/mol was observed to 600 °C. (The slow loss above 600 °C observed with both curves B and C is considered to be due to the slow decomposition of chromium(III) sulfate

$$Cr_2(SO_4)_3 \rightarrow Cr_2O_3 + 3SO_3 \qquad (16)$$

reported elsewhere.[1]) Even with excess chromate (2:1 mole ratio, Figure 3, curve D) there was some tendency for pyrosulfate to decompose (eq 5) as the weight loss to 600 °C was 13.5 g/mol of K_2CrO_4 (cf. 12 g/mol as calculated from eq 13 with a 2:1 mole ratio of reactants) and only 46 ± 1% of the original chromium had been precipitated as chromium(III) oxide.

Potassium chromate solutions were also reduced by sulfur dioxide to green insoluble chromium(III) oxide (a 6% SO_2/94% N_2 stream bubbled through an ~0.05 *m* solution for 2 h at 600 °C caused >98% reduction) but probably not via the acid–base reaction

$$2CrO_4^{2-} + SO_2 \rightarrow Cr_2O_7^{2-} + SO_3^{2-} \qquad (17)$$

since neither sulfide nor evolved sulfur was detected (the expected disproportionation/reaction products of sulfite[12]). A reduction analogous to that found in aqueous media

$$2CrO_4^{2-} + 3SO_2 \rightarrow Cr_2O_3 + 2SO_4^{2-} + SO_3 \qquad (18)$$

is considered more likely, probably via chromium(V) and/or chromium(IV), which have been shown to be the intermediates formed by many reducing agents. However thermogravimetric analysis confirmed that this reaction was not solely according to the stoichiometry of eq 18 but that the postulated reaction product, sulfur trioxide (which would form pyrosulfate by the reverse of reaction 5), was in competition for unreacted potassium chromate as in eq 13. For example, the weight gain of 127.5 mg from 2.2 mmol of K_2CrO_4 in 3 g of ternary eutectic exposed to 12% SO_2/88% N_2 (Figure 4, curve A), which was accompanied by the formation of the stoichiometric amount of insoluble chromium(III) oxide (166 mg), can be explained as 1.54 mmol of chromate reacting as eq 18 and 0.68 mmol with the sulfur trioxide produced (as eq 13). Thus of the 0.77 mmol of sulfur trioxide initially formed, 0.09 mmol would not have reacted and would be expected to be evolved, that is 7 mg, which compares well with the quantity of 5.5 mg found experimentally in the exit gas stream.

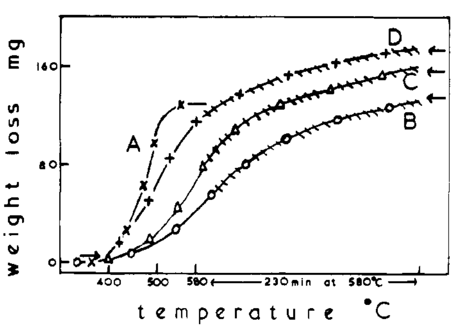

Figure 4. Thermogravimetric analysis in ternary sulfate eutectic (3 g) under sulfur dioxide (12%)/nitrogen (88%): A (×), 2.2 mmol of K_2CrO_4; B (○), 1.3 mmol of TiO_2, 3.2 mmol of $K_2S_2O_7$; C (△), 1.3 mmol of MoO_3, 3.2 mmol of $K_2S_2O_7$; D (+), 1.3 mmol of WO_3, 3.2 mmol of $K_2S_2O_7$. The arrows indicate the weight of evolved sulfur trioxide as estimated by titration.

When a 6% sulfur dioxide/air stream was 98% oxidized by the external catalyst converter (to SO_3) before passage through the chromate solution, reduction of the chromium (>98%) again occurred but much more rapidly. As expected in such acidic conditions, the product was a violet chromium(III) solution, formed by reactions equivalent to eq 5, 14, and 15.

Powdered chromium metal was insoluble and unreactive in the ternary sulfate eutectic at 580 °C, no gas being evolved or soluble chromium being found in the melt. On cooling, after 3 h at 580 °C, the undissolved solid was 99 ± 2% by weight of the original chromium. The absence of reproducible and reversible emf values of chromium electrodes (in Li_2SO_4/K_2SO_4 sulfate eutectic) was therefore unlikely to be due to macroscopic reaction as had been inferred,[24] though the slight darkening of the chromium observed after immersion in melt may represent a surface reaction. Additions of potassium pyrosulfate to the chromium metal in sulfate eutectic caused the metal to dissolve, forming an intensely violet solution of chromium(III), incidentally confirming the suggestion that pyrosulfate (or sulfur trioxide) is the corrosive entity in sulfate melts.[25]

Other Metals. Sulfur dioxide proved much less reactive with titanium(IV), niobium(V), molybdenum(VI), tantalum(V), and tungsten(VI). The oxides of these cations insoluble in ternary sulfate eutectic with the exception of molybdenum(VI) oxide,[1] showed no signs of reduction when sulfur dioxide was bubbled through the suspensions or solution. These oxides all dissolved when potassium pyrosulfate was present in the sulfate melt[1] but still gave no evidence of reduction even when exposed to sulfur dioxide, thus illustrating again the intrinsically greater stability

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(25) Burrows, B. W.; Hills, G. J. *Electrochim. Acta* **1970**, *15*, 445.

of the higher oxidation states of early transition metals and of the second- and third-row transition metals, as compared in this case to the reductions found with later first-row metals (Cr to Cu). Thermogravimetric analysis (Figure 4, curves B–D) showed these dissolved oxides in a sulfur dioxide/nitrogen atmosphere gave similar "stabilization of sulfur trioxide as pyrosulfate", as was found in nitrogen atmospheres.[1] In each case the experimentally determined weight of evolved sulfur trioxide (indicated by arrows in Figure 4) agreed well with the observed weight loss, showing that no sulfur trioxide had been formed by reduction reactions analogous to eq 18. All the observed sulfur trioxide could be accounted for by pyrosulfate decomposition (eq 5), but the slower weight loss when these transition-metal oxides were present suggested that the latter had dissolved to give cationic species, probably polymeric, which, though more thermally stable than pyrosulfate, ultimately decomposed to the same product. Similar stabilization had been observed when sulfur dioxide was not present.[1] This behavior is to be contrasted with that reported earlier in this paper, when iron(II) and manganese(II) caused more rapid decomposition of pyrosulfate, probably because the latter transition metals existed as nonpolymerized cations whose Lux–Flood acidity would be the most important factor in promoting decomposition.

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Registry No. SO_2, 7446-09-5; $CuSO_4$, 7758-98-7; Li_2SO_4, 10377-48-7; K_2SO_4, 7778-80-5; Na_2SO_4, 7757-82-6; Cu_2SO_4, 17599-81-4; $Fe_2(SO_4)_3$, 10028-22-5; $K_2S_2O_7$, 7790-62-7; $FeSO_4$, 7720-78-7; MnO_2, 1313-13-9; Na_2CO_3, 497-19-8; $K_2Cr_2O_7$, 7778-50-9; K_2CrO_4, 7789-00-6; TiO_2, 13463-67-7; MoO_3, 1313-27-5; WO_3, 1314-35-8; Cu, 7440-50-8.

Notes

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Tetraamine Complexes of Chromium(III). 5. Preparation of Bis(carboxylato)bis(1,2-ethanediamine)chromium(III) Complexes

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In 1970 Vaughn et al.[1] reported the preparation of *trans*-bis(acetato)bis(1,2-propanediamine)chromium(III) chloride monohydrate. Green et al.[2] used this method to prepare *trans*-bis(nicotinato-*O*)bis(1,3-propanediamine)chromium(III) chloride tetrahydrate. This method is now used to prepare some bis(carboxylato)bis(1,2-ethanediamine)chromium(III) complexes reported here.

Experimental Section

Preparation of Compounds. In a typical preparation, 15 g (0.056 mol) of commercial $CrCl_3·6H_2O$ (Baker Analyzed) and 0.30 mol of a carboxylic acid were mixed in 50 mL of distilled water. If the acid (such as benzoic acid and nicotinic acid) did not completely dissolve in water, a slurry was made by stirring with a magnetic stirrer. Then 50 mL (0.75 mol) of 1,2-ethanediamine was added dropwise to the mixture over a period of 45–60 min, the mixture being stirred constantly. After the addition of the amine, the mixture was heated to ca. 60 °C for 1 h and then evaporated on a steam bath in an evaporating dish until a solid crust formed on top of the liquid. After the mixture cooled to room temperature, any solid formed was filtered out and washed with a little absolute ethanol, followed by washing with acetone and drying in air. The propionic acid, isobutyric acid, 2,2-dimethylpropionic (pivalic) acid, benzoic acid, and nicotinic acid complexes were prepared; and the analytical results are summarized in Table I.

Analytical Methods. Chromium was determined as previously described,[3] and ionic chloride was determined by the method of Clarke[4] after ion-exchange chromatography, also as previously described.[5] Benzoate and nicotinate were determined by their UV spectra after chromatographing samples of the compounds on Na^+-form Dowex 50W-X8 columns and eluting the carboxylates with water. Carbon, nitrogen, and hydrogen were determined by H-M-W Laboratories, Phoenix, AZ.

Physical Measurements. The visible and UV spectra were measured by a Cary 14 or a Varian DMS 90 spectrophotometer, and the IR spectra were measured by a Perkin-Elmer Model 1500 FT-IR spectrophotometer, using KBr pellets of the compounds. Electrical conductances were measured by a Yellow Springs YSI Model 32 conductance meter.

Results and Discussion

In this work several aliphatic carboxylic acids were used in an attempt to prepare a variety of compounds, but only the complexes of propionic, isobutyric, and pivalic acids were successfully prepared. In the preparation of acetic, butyric, valeric, and isovaleric acid complexes, the reaction mixtures had colors (red-orange) similar to those of the other preparations; but no solid product was obtained.

The formulas of the compounds prepared are listed in Table I, based upon the elemental analyses. In contrast to the 1,3-propanediamine complexes,[1,2] the counterions of four of the five compounds prepared in this work were not chloride but the carboxylate anions. Molar conductance values (see Table II) indicated that all the compounds are 1:1 electrolytes, and the benzoate and nicotinate complexes have chromium to free carboxylate ratios of nearly 1 (1.07 and 1.04, respectively).

The IR spectra of the five compounds prepared showed shifts of the COO^- frequencies and the absence of the C=O stretching frequency characteristic of the carboxylic acids. For the propionate, isobutyrate, and pivalate complexes, $\nu_a(COO^-)$ of the carboxylate anion at ca. 1560 cm^{-1} was shifted to 1600–1620 cm^{-1} and $\nu_s(COO^-)$ at ca. 1450 and 1420 cm^{-1} were shifted to 1380–1395 and 1345–1360 cm^{-1}. For the benzoate complex, $\nu_a(COO^-)$ at 1595 cm^{-1} and $\nu_s(COO^-)$ at 1545 and 1410 cm^{-1} were shifted to 1605 cm^{-1} and to 1380 and 1353 cm^{-1}, respectively. These observations all indicate that the carboxylates are monodentate ligands.[6] For the nicotinate complex, however, $\nu_a(COO^-)$ was shifted from 1620 to 1612 cm^{-1} although the shift of $\nu_s(COO^-)$ from 1420 and 1324 cm^{-1} to 1380 and 1355 cm^{-1} was similar to those of the other complexes and the nicotinate complexes previously prepared.[7] Although the shift of $\nu_a(COO^-)$ to lower energy suggested bidentate ligation of the nicotinate anion, the analysis of the compound corresponds to three nicotinate anions per chromium atom, and the only formula that fits this analysis is a complex including two monodentate nicotinate anions and a third nicotinate as a counterion. The nicotinate counterion is confirmed by the chromium to free nicotinate ratio of 1.07.

The visible and UV spectra of the compounds in aqueous solutions are summarized in Table II. The spectra of *cis*- and *trans*-bis(acetato)bis(1,2-ethanediamine)chromium(III), reported by Nakahara,[8] are included for comparison. It can be seen that

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