sistent with the structure of the complexes of these bases with Bronsted acids. For example, the HCl–furan complex has been shown to involve hydrogen bond formation from HCl to the oxygen atom in the furan ring.[22] For the $ClF{\cdot}CH_3OH$ complex, a hydrogen-bonded complex might well be envisioned also. However, the key spectroscopic feature of such a complex would be a substantial red shift and intensification of the O–H stretching mode, as is characteristic of hydrogen-bonded species.[23] Such a spectral feature was not observed; rather, the only perturbed methanol vibration detected was the C–O stretch, supporting coordination at the oxygen atom. For the acetone complex, interaction of the fluoride portion of ClF with the carbonyl carbon must be considered, by analogy to the well-known catalytic attack of F^- at this site in solution. This type of interaction should lead to observable perturbation of the C–O stretch (as was observed) *and* the two C–C stretching modes. This was not observed, which lends support to interaction at the oxygen atom. This is probably due to the less polar nature of F in ClF relative to F^-. Further, the complex of HF with acetone has been shown[24] to involve hydrogenbond formation to the oxygen, rather than fluoride attack at the carbon (and HF is substantially more polar than ClF). The orientation of the ClF molecule cannot be directly determined, but the best dipole moment determinations all suggest a partial positive charge on the chlorine,[25,26] which would argue that the chlorine is oriented toward the oxygen atom. This result is in agreement with recent theoretical calculations on ClF complexes.[11-13]

The shift of the ClF stretching mode to lower energies is typical of halogen complexes; the halogens are σ^* acceptors, and acceptance of electron density from the Lewis base into the empty σ^* orbitals weakens the bond in the halogen diatomic.[1] This, in turn, leads to a lowering of the force constant and vibrational frequency of the complexed molecular halogen. The position of the ClF stretching mode in each of the complexes represents the degree of electron transfer to ClF from the particular base. Earlier studies of hydrogen-bonded complexes have correlated shifts with proton affinity and dipole moment of the bases. Table I presents a series of such comparisons, from which it can be seen that proton affinity qualitatively predicts the observed trends in $\Delta\nu_{ClF}$. The dipole moment of the base fares rather poorly in such a comparison, probably because the dipole moment reflects the electronic distribution over the entire molecule, while the proton affinity reflects more directly the electronic distribution in the region of the oxygen atom, where interaction occurs. The proton affinity correlation is not perfectly monotonic, but does provide a relatively good measure of the strength of interaction of a reference acid, ClF in this case, with a series of Lewis bases.

The 1/1 complexes of oxygen-containing bases with both Lewis and Brønsted acids have been studied over the years; comparison of the spectral features of these complexes with the ClF complexes observed here help to provide information about the Lewis acidity of ClF (as opposed to its reactivity). The symmetric C–O–C stretching mode of dimethyl ether has emerged as a particular useful vibrational mode in this regard; this mode was observed at 917 cm^{-1} in the 1/1 complex with SiF_4,[17] at 892 cm^{-1} with GeF_4[18] and at 884 cm^{-1} with BBr_3.[27] The observation of this mode at 904 cm^{-1} in the present ClF study indicates that the Lewis acidity of ClF roughly falls between that of GeF_4 and that of SiF_4, a conclusion which is substantiated by comparison of the spectra of acetone complexes of these acids.[18,28] While this cannot provide a quantitative measure, such as fluoride ion affinity does, it does provide some indication of strength of ClF as a Lewis acid, information which has not previously been available. Larson and McMahon have recently discussed gas-phase Lewis acidities thoroughly, and the results obtained here should be put in the context of that work also.[29]

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Molten Lithium Sulfate–Sodium Sulfate–Potassium Sulfate Eutectic: Lux–Flood Acid–Base Reactions of Transition-Metal Sulfates and Oxides

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The solubility and reactivity of seven first-row transition-metal sulfates in the ternary eutectic (78 mol % Li_2SO_4, 8.5 mol % Na_2SO_4, 13.5 mol % K_2SO_4) and in the ternary eutectic containing sodium carbonate have been studied and the transition-metal oxide products identified. The reactions of six, more acidic, transition-metal oxides with pure melt and with added sodium carbonate were studied and stoichiometries established. Additions of potassium pyrosulfate dissolved all the oxides, in some cases with reduction (to Mn(II) and Co(II)), and the thermal stabilities of the resulting solutions were determined.

Introduction

Molten sulfates are of considerable economic importance because they form the reactive films causing the corrosion of high-temperature boilers and heat exchangers. Thus a systematic chemistry of transition metals in such solutions has a considerable practical relevance, as it also has to the catalysts promoting the oxidation of sulfur dioxide by air in the manufacture of sulfuric acid, which primarily consist of vanadium solutions but also contain transition metals as "promotors". However until now little work has been published on acidic–basic reactions of transition metals, and a more systematic study seemed overdue.

The earlier references to acid–base reactions in molten alkali-metal sulfates (using the Lux–Flood definition of acids as oxide acceptors) began with the work of Lux himself, who reported the reactions of titanium(IV) oxide as an acid in sodium sulfate at 950 °C when a series of titanates was formed.[1] More recently

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Table I. Solubility at 580 °C and Thermogravimetry of Transition-Metal Sulfates in the Ternary Sulfate Eutectic

			TG with sulfate melt					TG of reactant alone				
reactant	color of solution	solubility, *m*	temp of reacn, °C start	finish	product	exptl wt loss, g/mol	calcd wt loss, g/mol	temp of reacn, °C start	finish	product	exptl wt loss, g/mol	calcd wt loss, g/mol
$MnSO_4$	colorless	>0.36 m	830	>950	Mn_3O_4			710	870	Mn_3O_4	74.0 ± 0.5	74.6
$FeSO_4$	yellow-brown		570	950	α-Fe_2O_3	71.0 ± 0.5	72.0	500	730	α-Fe_2O_3	71.0 ± 0.5	72.0
$Fe_2(SO_4)_3$	red-brown		550	950	α-Fe_2O_3	238 ± 1	240	510	690	α-Fe_2O_3	237 ± 1	240
$CoSO_4$	deep blue	>0.31	800	>950	CoO			690	860	Co_3O_4	75 ± 0.5	74.6
$NiSO_4$	rose-red	>0.27	740	>950	NiO	80.0 ± 1	80	650	840	NiO	79.0 ± 1	80
$CuSO_4$	green	>0.31	630	>950	$CuO\cdot CuSO_4$[a]			590	705	$CuO\cdot CuSO_4$	40.0	40
					CuO[a]			590	790	CuO	79.0 ± 1	80
					$CuSO_4$[a]							
					$CuSO_4$[b]							
					Cu_2O[b]							

[a] Quenched at 800 °C. [b] Quenched at 900 °C.

niobium(V) oxide has been found to react at similar temperatures in the ternary eutectic used here to form metaniobates[2] and iron(III) oxide to be dissolved in potassium sulfate melts containing potassium pyrosulfate.[3] There are also a number of scattered references to oxidation–reduction reactions and to the spectroscopy of transition-metal compounds in molten sulfate, but these will be considered in later papers concerned with those aspects of transition-metal chemistry in molten sulfates.

Experimental Section

Materials. The ternary eutectic, sodium carbonate, and potassium pyrosulfate were prepared as previously reported.[4] Reagent grade oxides (Cr_2O_3, TiO_2, MnO_2, Nb_2O_5, WO_3) were dried at 110 °C for 2 h, as was tantalum(V) oxide (AnalaR). AnalaR molybdenum(VI) oxide was dried at 200 °C for 4 h. Hydrated transition-metal sulfates (AnalaR (AR) or reagent grade (RG)) were dehydrated under the conditions given by Duval[5] and analyzed ($Cr_2(SO_4)_3\cdot 15H_2O$ (RG) 2 h at 470 °C. Found: Cr, 26.3; SO_4^{2-}, 72.6. Calcd for $Cr_2(SO_4)_3$: Cr, 26.6; SO_4, 73.4. $MnSO_4\cdot 4H_2O$ (AR) 3 h at 350 °C. Found: Mn, 36.1; SO_4, 63.2. Calcd for $MnSO_4$: Mn, 36.4; SO_4, 63.6. $FeSO_4\cdot 7H_2O$ (AR) 4 h at 300 °C under N_2. Found: Fe, 37.1. Calcd for $FeSO_4$: Fe, 36.8. $Fe_2(SO_4)_3$ (RG) 2 h at 300 °C. Found: Fe, 27.3; SO_4, 71.2. Calcd for $Fe_2(SO_4)_3$: Fe, 28.0; SO_4, 72.0. $CoSO_4\cdot 7H_2O$ (AR) 2 h at 400 °C. Found: Co, 37.6; SO_4, 61.6. Calcd for $CoSO_4$: Co, 38.0; SO_4, 62.0. $NiSO_4\cdot xH_2O$ (AR) 2 h at 450 °C. Found: Ni, 37.7; SO_4, 61.6. Calcd for $NiSO_4$: Ni, 38.0; SO_4, 62.0. $CuSO_4\cdot 5H_2O$ (AR) 2 h at 250 °C. Found: Cu, 39.3; SO_4, 59.9. Calcd for $CuSO_4$: Cu, 39.8; SO_4, 60.2).

Procedure. Qualitative reactions and thermogravimetry under air, nitrogen, or carbon dioxide atmospheres were carried out as previously described.[4] Products were identified by conventional tests on gas effluents or aqueous solutions made from solidified reacted melts and by X-ray powder diffraction of solid products as previously described.[4]

Results and Discussion

Chromium(III) sulfate dissolved in the ternary sulfate eutectic at 580 °C to give an intense violet solution, which however was not stable but decomposed over several days, evolving sulfur trioxide and forming a green precipitate (Found: Cr, 67.7. Calcd for Cr_2O_3: Cr, 68.4). On the thermobalance this decomposition could be detected from 520 °C (Figure 1, curve A) but was very slow below 800 °C. At 950 °C the total loss was 242 g/mol of $Cr_2(SO_4)_3$ (calculated weight loss 240 g/mol of $Cr_2(SO_4)_3$) corresponding to

$$Cr_2(SO_4)_3 \rightarrow Cr_2O_3 + 3SO_3 \qquad (1)$$

and less than 1% of the chromium(III) had been oxidized to chromium(VI). When no sulfate eutectic was present, a similar reaction occurred but at much lower temperatures (Figure 1, curve B). In this case the total weight loss was 234 g/mol of $Cr_2(SO_4)_3$, and the composition of the residue was confirmed by X-ray diffraction (*d* spacings are 2.65 (100), 2.48 (80), 3.62 (60); ASTM Index for Cr_2O_3 is 2.67 (100), 2.48 (90), 3.63 (75)).

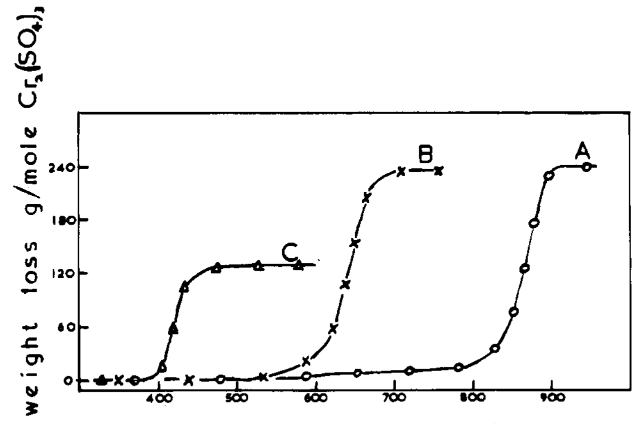

Figure 1. Thermogravimetric analysis of chromium(III) sulfate in air: A (○), 0.45 *m* in ternary sulfate eutectic; B (×), 0.39 g alone; C (△), 0.50 *m* with 1.5 *m* Na_2CO_3 in ternary sulfate eutectic.

This stabilization of chromium(III) in molten sulfate solution is characteristic of that found with all dissolved transition-metal cations and is attributed largely to the effects of solvation by sulfate, though in addition any sulfur trioxide produced will tend to form pyrosulfate, which will facilitate the reverse reaction of eq 1, i.e.

$$Cr_2O_3 + 3K_2S_2O_7 \rightarrow Cr_2(SO_4)_3 + 3K_2SO_4 \qquad (2)$$

Addition of sodium carbonate to chromium(III) sulfate dissolved in the eutectic at 580 °C resulted in evolution of carbon dioxide and immediate precipitation of green chromium(III) oxide. The precipitate could be redissolved by addition of potassium pyrosulfate, and the violet solution was re-formed. Thermogravimetry showed the reaction with sodium carbonate to take place quite largely in the solid state (Figure 1, curve C), with 3:1 reactant ratios (Na_2CO_3:$Cr_2(SO_4)_3$), and with excess carbonate the weight losses corresponded to 130 ± 0.5 g/mol of $Cr_2(SO_4)_3$, but with a ratio of <3:1 they corresponded to 44.0 ± 0.5 g/mol of Na_2CO_3 (calculated weight loss 132 g/mol of $Cr_2(SO_4)_3$ and 44.0 g/mol of Na_2CO_3), supporting equation 3. When added directly to

$$Cr_2(SO_4)_3 + 3Na_2CO_3 \rightarrow Cr_2O_3 + 3Na_2SO_4 + 3CO_2 \qquad (3)$$

sulfate melt, chromium(III) oxide was insoluble and unreactive, no weight loss being detected up to 900 °C. While pyrosulfate would dissolve the oxide to form the violet chromium(III) solution, sodium carbonate additions produced no effect, indicating the very low Lux–Flood acidity of chromium(III) oxide, which is however known to react with bases at temperatures above 950 °C to form chromites (chromate(III)) and/or to oxidize to chromate(VI)).

Six other first-row transition-metal sulfates were then examined in the same manner; the observations on their solubility together with results of thermogravimetry carried out on molten sulfate

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Table II. Reaction at 580 °C and Thermogravimetry in Air of Transition-Metal Sulfates with Sodium Carbonate in the Ternary Sulfate Eutectic

	reacn at 580 °C		thermogravimetry for 1:1 MSO_4:Na_2CO_3 ratio				
			temp of reacn, °C				
reactant	color of insoluble product	product[a]	start	finish	product[a]	exptl wt loss, g/mol	calcd wt loss, g/mol
$MnSO_4$	green-brown	MnO	410	490	Mn_3O_4	38.5 ± 0.5	38.7
	dark brown[b]	Mn_3O_4[b]	405	510	MnO[c]	43.0 ± 0.5[c]	44.0[c]
$CoSO_4$	green	CoO	390	520	Co_3O_4	38.0 ± 0.5	38.7
	black[b]	Co_3O_4[b]	390	470	CoO[c]	43.5 ± 0.5[c]	44.0[c]
$NiSO_4$	green	NiO	410	500	NiO	44.0 ± 0.5	44.0
$CuSO_4$	black	CuO	315	490	CuO	43.5 ± 0.5	44.0

[a] Product indicated by X-ray powder diffraction. [b] Trace only. [c] Under nitrogen atmosphere.

Table III. Quantities of Transition-Metal Oxide Product Produced from Additions of Sodium Carbonate to Various Concentrations of Transition-Metal Sulfate in the Ternary Sulfate Eutectic at 580 °C

reactants			products	
MSO_4	quant, mmol	Na_2CO_3, mmol	MO	quant, mmol
$CoSO_4$	1.82	1.29	CoO	1.27
	1.54	2.03		1.53
	3.10	2.19		2.18
$NiSO_4$	1.16	0.62	NiO	0.61
	1.05	1.42		1.04
	2.70	1.45		1.47
$CuSO_4$	1.27	1.53	CuO	1.24
	3.08	1.34		1.33
	2.51	2.03		2.00

solutions, and for comparison on the transition-metal compounds without melt, are given in Table I. The solid products containing transition metals were identified by X-ray powder diffraction on the washed and dried precipitates except in the case of copper when the quenched melts were used and lines for the alkali-metal sulfates were discounted. The thermogravimetric curves were similar in general shape to those in Figure 1, the temperatures at which weight loss became measurable and at which weight loss ceased being given in Table I. The considerable stabilization of transition-metal cations when dissolved in sulfate melt, as compared to that of the transition-metal sulfate alone, is again clearly seen, though the cations do react as Lux–Flood acids at higher temperatures. As expected the more highly charged (3+) cations show the higher reactivity (however Fe^{3+} is considerably more reactive than Cr^{3+}), and the divalent cations follow the order of reactivity $Fe^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$, which is the same order as for the sulfates when heated alone and has been observed previously.[6]

The position of iron(II) in this order may have been affected by its easy oxidation, since after 1 h at 580 °C in an air atmosphere about 3% of an initially 0.1 *m* solution was oxidized to iron(III). Oxidation still occurred, but was perhaps slightly slower, under a nitrogen atmosphere. However after longer times in air oxidation was largely complete (e.g. 80% of a 0.1 *m* solution after 2 days at 580 °C), and a red-brown precipitate formed (Found: Fe, 69.0. Calcd for Fe_2O_3: Fe 69.9). Tests on the latter solutions for sulfur, sulfite and sulfide were negative, suggesting, as did the thermogravimetric results, that the oxidation of iron(II) was largely by sulfate, rather than by air directly, and that reduction of sulfate stopped at sulfur(IV), i.e.

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3 \quad (4)$$

(calculated weight loss 72 g/mol of $FeSO_4$), which is in accord with the conclusion of Burrows and Hills[7] that the most likely reduction products from oxidation by sulfur trioxide would be sulfur dioxide and oxide. Similarly formation of the other transition-metal oxides is considered to have involved oxidation by sulfate, rather than by air, since the experimental weight losses agree very well with

$$3MnSO_4 \rightarrow Mn_3O_4 + SO_2 + 2SO_3 \quad (5)$$

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3 \quad (6)$$

$$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3 \quad (7)$$

$$3CoSO_4 \rightarrow Co_3O_4 + SO_2 + 2SO_3 \quad (8)$$

$$NiSO_4 \rightarrow NiO + SO_3 \quad (9)$$

With $NiSO_4$ the equilibrium weight loss was obtained after it was heated at 970 °C for $2^1/_2$ h.

$$2CuSO_4 \rightarrow CuO \cdot CuSO_4 + SO_3 \quad (10)$$

$$CuSO_4 \rightarrow CuO + SO_3 \quad (11)$$

Here it may be noted that copper(II) oxide is unstable above 800 °C with loss of oxygen and formation of copper(I) oxide, whose X-ray diffraction lines were found in the sample quenched from 900 °C. Likewise the formation of cobalt(II) oxide in the reaction of cobalt(II) sulfate in sulfate melt in an air atmosphere below 900 °C may be noted as contrasting with the formation of the higher oxide (Co_3O_4) when no melt is present. This formation of the lower oxide again demonstrates the low solubility of oxygen in the sulfate melt.

The reactions of these transition-metal sulfate solutions with added sodiumn carbonate are summarized in Table II. The thermogravimetric curves indicate that reactions in the presence of the stronger Lux–Flood base (Na_2CO_3) were again at much lower temperatures than in molten sulfate alone and were largely completed before melting, the temperatures of commencement and cessation of weight loss being given in Table II. After melting, these insoluble transition-metal products and the products produced by reaction at 580 °C were all redissolved when potassium pyrosulfate was added, forming solutions of the colors listed in Table I, i.e.

$$MO + K_2S_2O_7 \rightarrow MSO_4 + K_2SO_4 \quad (12)$$

The weights of oxide product produced from various ratios of reactants (Table III) give additional support to the thermogravimetric results that the major reactions could be represented by

$$MSO_4 + Na_2CO_3 \rightarrow MO\downarrow + Na_2SO_4 + CO_2 \quad (13)$$

However in air on the thermobalence both manganese(II) sulfate and cobalt(II) sulfate formed the higher oxides (Mn_3O_4 and Co_3O_4); traces of the same oxides were also found in the products of the isothermal reaction at 580 °C. Although manganese(II) oxide has been reported to be oxidized by carbon dioxide above 400 °C[8]

$$3MnO + CO_2 \rightarrow Mn_3O_4 + CO \quad (14)$$

here air is considered to be the major oxidant, particularly in the thermogravimetric analyses where it had easy access before the solid mixture melted, since little oxidation took place under a nitrogen atmosphere (Table II).

Manganese(IV) oxide was found to be insoluble and unreactive both in the sulfate eutectic alone at 580 °C and when sodium

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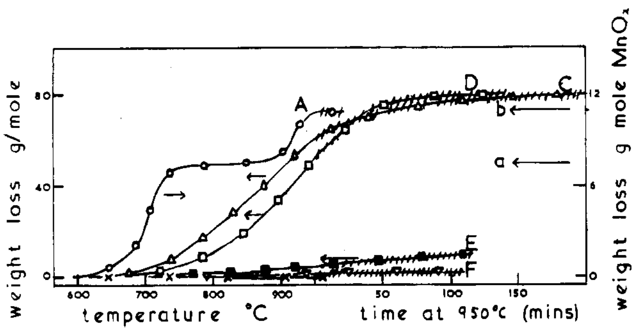

Figure 2. Thermogravimetric analyses of transition-metal oxides in the ternary sulfate eutectic: A (○), 1.0 *m* MnO_2 in air (right-hand scale); B (×), 0.33 *m* TiO_2 in nitrogen (left-hand scale); C (△), 0.33 *m* MoO_3 in nitrogen (left-hand scale); D (□), 0.33 *m* WO_3 in nitrogen (left-hand scale); E (■), 0.33 *m* Nb_2O_5 in nitrogen (left-hand scale); F (▽), 0.33 *m* Ta_2O_5 in nitrogen (left-hand scale).

carbonate was present. No gas was evolved, and 98% of the carbonate was still present after 1 h, indicating it was of insufficient basicity to cause a reaction such as

$$MnO_2 + Na_2CO_3 \rightarrow Na_2MnO_3 + CO_2 \quad (15)$$

However addition of potassium pyrosulfate caused the manganese(IV) oxide to dissolve to a colorless solution of manganese(II)

$$MnO_2 + K_2S_2O_7 \rightarrow MnSO_4 + K_2SO_4 + {}^1/_2O_2 \quad (16)$$

a reduction analogous to that found in molten nitrates[9] where the manganese(IV)/manganese(II) equilibrium is displaced toward the latter oxidation state in acidic melt solutions. At higher temperatures manganese(IV) oxide evolved oxygen, the thermogram (Figure 2, curve A) indicating two reactions corresponding to

$$2MnO_2 \rightarrow Mn_2O_3 + {}^1/_2O_2 \quad (17)$$

(calculated weight loss 8.0 g/mol; line a on curve A of Figure 2 indicating an experimental weight loss of 7.5 ± 0.5 g/mol of MnO_2) and

$$3MnO_2 \rightarrow Mn_3O_4 + O_2 \quad (18)$$

(calculated weight loss 10.7 g/mol; line b on curve A of Figure 2 indicating an experimental weight loss of 11.0 ± 0.5 g/mol of MnO_2).

The reactions of five other transition-metal oxides (TiO_2, MoO_3, WO_3, Nb_2O_5, Ta_2O_5) were also examined. All were insoluble in the ternary sulfate eutectic at 580 °C, except molybdenum(VI) oxide, which slowly dissolved to give a yellow solution, though the more acidic oxides (MoO_3, WO_3) reacted at higher temperatures giving weight losses (Figure 2, curves C and D) of 80 g/mol, equivalent to the formation of orthomolybdate and orthotungstate.

$$MO_3 + SO_4^{2-} \rightarrow MO_4^{2-} + SO_3 \quad (19)$$

The other oxides gave much smaller weight losses (Figure 2, curves B, E, and F) diminishing, as expected, in order of their Lux–Flood acidity.

$$Nb(V) > Ta(V) > Ti(IV)$$

However, again as expected, their acidity was more apparent when sodium carbonate was present, though the temperatures at which reaction ceased (510 °C for formation of MoO_4^{2-}, 520 °C for WO_4^{2-}, 690 °C for NbO_4^{3-}, 960 °C for TaO_4^{3-}, 540 °C for $Nb_4O_{11}^{2-}$, 690 °C for TaO_3^-, 800 °C for TiO_3^{2-}) followed the same order of acidity. The temperatures of onset of reaction were less regular (390 °C for MoO_3, 460 °C for WO_3, 460 °C for TiO_2, 510 °C for Ta_2O_5, and 520 °C for Nb_2O_5), since this was often when the mixtures were still nominally solid, though the lowering of the melting point varied with the particular solutes/products present. These and subsequent reactions were carried out under a carbon dioxide atmosphere, which prevented thermal decomposition of carbonate to 950 °C (which otherwise became appreciable above 600 °C in air). The products formed, which all gave colorless solutions in sulfate melt at 580 °C, were in accordance with

$$TiO_2 + CO_3^{2-} \rightarrow TiO_3^{2-} + CO_2 \quad (20)$$

(calculated weight loss 44 g/mol of TiO_2)

$$MoO_3 + CO_3^{2-} \rightarrow MoO_4^{2-} + CO_2 \quad (21)$$

$$WO_3 + CO_3^{2-} \rightarrow WO_4^{2-} + CO_2 \quad (22)$$

(calculated weight loss 44 g/mol of MO_3).

In the case of titanium no sign was found on the thermogravimetric curve of the intermediate titanates (e.g. $Na_2Ti_2O_5$ and $Na_8Ti_{15}O_{14}$) reported in the high-temperature reaction of titanium(IV) oxide with alkali-metal carbonates,[10,11] though the small additional weight loss found with higher ratios of sodium carbonate (≥2 mol/mol of TiO_2 at 950 °C) may indicate that slow formation of more basic titanates (e.g. $Na_6Ti_2O_7$ and Na_4TiO_4), which have been claimed to form above 800 °C.[12]

With molybdenum(VI) and tungsten(VI) oxides it is noteworthy that the reaction temperature was much lower than the 800–1000 °C found in the absence of sulfate melt,[13] but more basic anions (MO_5^{4-}) obtained by heating with excess carbonate[14,15] at 610/650 °C did not seem to be formed probably because such anions were not stable in the carbon dioxide atmosphere used.

Niobium(V) and tantalum(V) oxides being less acidic reacted at rather higher temperatures, and the weight losses with varying ratios of sodium carbonate indicated the formation of a series of oxyanions

$$M_2O_5 + CO_3^{2-} \rightarrow 2MO_3^- + CO_2 \quad (23)$$

$$M_2O_5 + 2CO_3^{2-} \rightarrow M_2O_7^{4-} + 2CO_2 \quad (24)$$

$$M_2O_5 + 3CO_3^{2-} \rightarrow 2MO_4^{3-} + 3CO_2 \quad (25)$$

(calculated weight losses 44, 88, and 132 g/mol of M_2O_5 respectively), of which metaniobate[2,16] (NbO_3^-), orthoniobate[17,18] (NbO_4^{3-}), and orthotantalate[17,18] (TaO_4^{3-}) are well substantiated in the literature. With higher ratios of sodium carbonate small weight losses above 670 °C with niobium(V) oxide may indicate some further reaction, but no horizontal was reached, though with tantalum(V) oxide the formation of a more basic tantalate was indicated

$$2Ta_2O_5 + 9Na_2CO_3 \rightarrow Na_{18}Ta_4O_{19} + 9CO_2 \quad (26)$$

(calculated weight loss 198 g/mol of Ta_2O_5), probably related to those ($Na_{12}Ta_4O_{16}$, $Na_8Ta_6O_{19}$) already reported.[19]

When each of these five oxides was added to the sulfate eutectic containing potassium pyrosulfate at 580 °C, they dissolved to colorless solutions and some sulfur trioxide was evolved. Thermogravimetry (Figure 3) showed that the temperatures of evolution of equivalent amounts of sulfur trioxide were considerably

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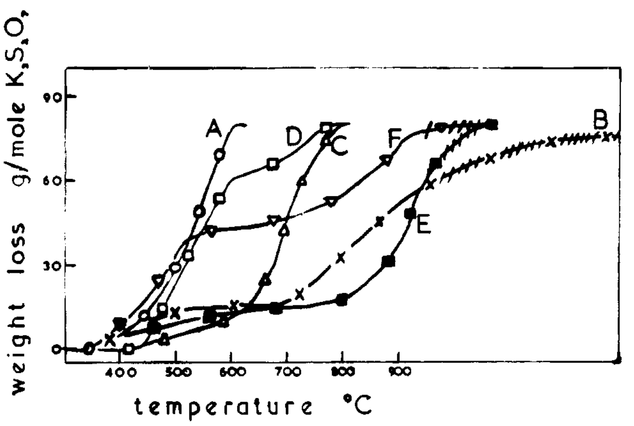

Figure 3. Thermogravimetric analysis of potassium pyrosulfate, and of transition-metal oxides with potassium pyrosulfate, in the ternary sulfate eutectic under nitrogen: A (○), 0.33 *m* $K_2S_2O_7$; B (×), 0.33 *m* TiO_2 + 0.33 *m* $K_2S_2O_7$; C (△), 0.33 *m* MoO_3 + 0.33 *m* $K_2S_2O_7$; D (□), 0.33 *m* WO_3 + 0.33 *m* $K_2S_2O_7$; E (■), 0.33 *m* Nb_2O_5 + 0.33 *m* $K_2S_2O_7$; F (▽), 0.33 *m* Ta_2O_5 + 0.33 *m* $K_2S_2O_7$.

higher than with only pyrosulfate in the sulfate melt (cf. Figure 3, curve A) and thus in terms of the sulfuric acid catalyst that sulfur trioxide was considerably stabilized in the presence of these transition-metal oxides. Though in each case the appropriate amount of sulfur trioxide was evolved at a sufficiently high temperature, i.e.

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_3 \qquad (27)$$

(calculated weight loss 80 g/mol of $K_2S_2O_7$), the order of stabilization varied considerably with temperature, being Ta < W < Ti < Nb < Mo at 500 °C but W < Ta < Mo < Ti < Nb at 700 °C. The delay of weight loss with molybdenum and tungsten oxide to 430 °C (curves C and D) indicated that interaction of pyrosulfate and the metal oxide had occurred below 340 °C (the decomposition temperature of $K_2S_2O_7$ in the sulfate eutectic) while the closely similar decomposition of pyrosulfate alone (curve A) and with tantalum oxide (curve F) up to 500 °C suggested that interaction only commenced at this temperature. Before decomposition, the colorless solutions presumably contained nominally cationic transition-metal species, though by analogy with their aqueous chemistry these may not have been monomeric (e.g. MoO_2^{2+}) but polymeric (e.g. $(TiO)_n^{2+}$). In either case their thermal stability (cf. Figure 1 and Table I) suggests that considerable coordination by sulfate anions would be expected, with the metals probably also joined by oxo bridges. Such chains, or three-dimensional polymers, (sulfates can be bidentate and bridging), which are such a noteworthy feature of vanadium solutions in sulfate melts, may well be important in the performance of the sulfuric acid catalysts.

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Registry No. Li_2SO_4, 10377-48-7; Na_2SO_4, 7757-82-6; K_2SO_4, 7778-80-5; Cr_2O_3, 1308-38-9; TiO_2, 13463-67-7; MnO_2, 1313-13-9; Nb_2O_5, 1313-96-8; WO_3, 1314-35-8; Ta_2O_5, 1314-61-0; MoO_3, 1313-27-5; $Cr_2(SO_4)_3$, 10101-53-8; $MnSO_4$, 7785-87-7; $FeSO_4$, 7720-78-7; $Fe_2(SO_4)_3$, 10028-22-5; $CoSO_4$, 10124-43-3; $NiSO_4$, 7786-81-4; $CuSO_4$, 7758-98-7; $K_2S_2O_7$, 7790-62-7; Na_2CO_3, 497-19-8.

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Resonance Raman and Surface-Enhanced Resonance Raman Scattering Studies on Electrochemical Redox Processes of Iron Tetrakis(*N*-methyl-4-pyridiniumyl)porphine

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The electrochemical reduction processes of iron(III) tetrakis(*N*-methyl-4-pyridininiumyl)porphine ($Fe^{III}TMPyP$) at pH 1.0 (in 0.1 N H_2SO_4) and 10.5 (in 0.1 N K_2SO_4 + KOH) were followed by resonance Raman spectroscopy. On conversion from the ferric complex to the ferrous one at pH 1.0 the Raman band mainly due to the C_β–C_β stretching vibration and that due to the C_α–N stretching vibration shift from 1557 to 1547 cm^{-1} and from 1363 to 1345 cm^{-1}, respectively. Similar frequency shifts were observed for the reduction at pH 10.5. From these results it was concluded that the reduction of the metalloporphine proceeds in a high-spin state at both pHs. The redox processes of FeTMPyP adsorbed at Ag electrode surfaces were also studied by surface-enhanced resonance Raman spectroscopy. The SERS + RRS spectra observed at −0.1 and −0.35 V (vs. Ag/AgCl) for the adsorbate from the solution of FeTMPyP in 0.1 M Na_2SO_4 (pH 5.6) are almost the same as the RRS spectra of the ferric and ferrous porphines in the bulk solution, respectively. At pH 1.0 (in 0.1 N H_2SO_4) the adsorbate, which gives rise to the SERS + RRS spectrum characteristic of the ferrous complex at −0.15 V, shows a marked change in the surface spectrum on sweeping the electrode potential to +0.135 V. This change can be interpreted as arising from an elimination process of the central iron atom from the complex. The surface spectra observed under various conditions at pH 1.0 proved that a reversible elimination–incorporation process of the central iron atom is taking place at the electrode surface in the potential range of −0.15–+0.135 V.

Introduction

Electrochemical properties of metalloporphines have been studied by using a variety of methods.[1] Notably iron porphyrins in bulk solutions and those on electrode surfaces are of special interest because of their biological importance and catalytic properties.[2] Several recent publications indicated that resonance Raman scattering (RRS) spectroscopy with the combined use of an electrochemical system is very useful for elucidating the structural changes accompanied by the redox reactions of metalloporphines.[3] Surface-enhanced resonance Raman scattering (SERS + RRS) spectroscopy is expected to be very useful to understand the reactions taking place on electrode surfaces.[4] The application of these methods has been previously demonstrated for water-soluble porphines such as *meso*-tetrakis(4-sulfonatophenyl)porphine (TSPP),[5,6] *meso*-tetrakis(4-carboxyphenyl)por-

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