Thermochimica Acta, 121 (1987) 121–135
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOGRAVIMETRIC INVESTIGATION OF REACTIONS BETWEEN VANADIUM(V) COMPOUNDS AND PYROSULPHATE IN ALKALI METAL SULPHATE MELTS *

R.I. DEARNALEY and D.H. KERRIDGE

Department of Chemistry, The University, Southampton SO9 5NH (Gt. Britain)

(Received 19 September 1986)

ABSTRACT

The interactions between sulphate, pyrosulphate, vanadium pentoxide, metavanadate and orthovanadate have been studied thermogravimetrically and were shown to be strongly dependent on the alkali metal present, the smaller and more polarising cations causing decomposition of pyrosulphate (to SO_3) at lower temperatures.

Sulphate and vanadium pentoxide were found to have a stabilising effect on pyrosulphate, thought to be due to the formation of vanado-sulphato polymers, an explanation which received support from infrared spectroscopy. The physical nature of the melts (i.e. whether viscous or mobile, and the formation of solid crusts on liquid melts) influenced the rates of weight loss.

The results enabled the behaviour of the contact catalyst for sulphuric acid manufacture to be more completely understood.

INTRODUCTION

The contact catalyst used for the production of sulphuric acid by oxidation of sulphur dioxide to sulphur trioxide, consists of vanadium oxides dissolved in alkali metal pyrosulphate/sulphate melts supported on a porous siliceous material, often kieselguhr. Despite extensive investigation of phase diagrams of vanadium pentoxide with alkali metal sulphates [1,2], with pyrosulphates [3,4] and of the kinetics of interactions between these systems and sulphur dioxide/sulphur trioxide/air mixtures [5,6], the stable species formed by these reagents are not yet certain and indeed more have been reported recently [7–12]. In aqueous media, vanadium(V) is known to form a series of species depending on the concentration of vanadium and on the

---

* Dedicated to Professor W.W. Wendlandt on the occasion of his 60th birthday. The authors, and in particular the senior author, are most grateful to Professor W.W. Wendlandt for his unfailing encouragement and courtesy over many years. We wish him a very happy birthday and many more years of distinguished thermoanalytical chemistry.

0040-6031/87/$03.50 © 1987 Elsevier Science Publishers B.V.

TABLE 1

Composition of samples (mmol) and temperature of onset of discernible weight loss

Mixture	V_2O_5	$NaVO_3$	$K_2S_2O_7$	$Na_2S_2O_7$	Li_2SO_4	Na_2SO_4	K_2SO_4	Weight of ternary eutectic (g)	Temperatures of weight loss (°C)
1	1				1				400 [a]
2	1					1			640 [a]
3	1						1		600 [a]
4	1		1						300
5	1		1				$\frac{1}{2}$		470
6	1		1				1		400 [b]
7	1		1				2		560
8	1		1				4		550 [c]
9	1		1			1			450
10	1		1			2			400 [b]
11	1		1		2				340
12	1		1		$\frac{1}{2}$		$\frac{3}{2}$		520
13	1			1					340
14	1			1		1			470
15	1			1		2			530
16	1		2						300
17	1		2				2		420

18	1		2				4		350 [b,c]
19		2						2	> 900
20	1							2	680 [a]
21		2	1					2	700
22	1		$\frac{1}{2}$					2	580 [a]
23	1		1					2	570 [a]
24		2	2					2	560
25	1		$\frac{4}{3}$					2	340 [a]
26	1		$\frac{3}{2}$					2	340 [a]
27	1		2					2	340 [a]
28		2	3					2	360
29			1					2	340 [a]
30			1						400 [a]
31			1		2				340 [a]
32			1			2			400 [a]
33			1				10		400 [a]
34				1					370 [a]
35				1		2			370 [a]
36	(1 mmol Na_3VO_4)		$1\frac{3}{4}$					2	340

---

[a] Heating rate 2° C min^{-1}, otherwise 4° C min^{-1}.

[b] <1 mg lost to 500° C.

[c] Very viscous system.

acidity of the system [13], but little is known about such equilibria in molten sulphate and/or pyrosulphate media.

In a previous study [14] of Lux–Flood acid–base reactions, vanadium pentoxide was reported to dissolve in the ternary sulphate eutectic melt (Li_2SO_4, 78 mol%; Na_2SO_4, 8.5%; K_2SO_4, 13.5%; m.p., 512°C [15]) and several vanadate(V) compounds were formed after reaction with different ratios of base (Na_2CO_3). The current work complements this study and is concerned with a thermogravimetric investigation of the relative stabilities, with respect to loss of sulphur trioxide, of mixtures of vanadium(V) compounds with alkali metal pyrosulphates (Lux–Flood acids) in various sulphate melts under air atmospheres.

EXPERIMENTAL

Lithium sulphate, sodium sulphate and potassium sulphate (all BDH AnalaR) were dried at 200°C for 2 h and the ternary sulphate eutectic ($Li_2SO_4 : Na_2SO_4 : K_2SO_4$; 78 : 8.5 : 13.5 mol%; melting point, 512°C [15]) was prepared as described previously [16]. The binary eutectic (Li_2SO_4: Na_2SO_4; 63.3 : 36.7 mol%; m.p., 586°C) was prepared similarly. Vanadium pentoxide and sodium metavanadate were dried at 110°C for 2 h. Sodium orthovanadate was dried at 250°C for 2 h. Potassium pyrosulphate was prepared in situ from potassium persulphate (BDH AnalaR) which decomposes above 200°C according to the equation:

$$2K_2S_2O_8 \rightarrow 2K_2S_2O_7 + O_2$$

Sodium pyrosulphate was prepared by heating BDH AnalaR sodium hydrogen sulphate firstly at 120°C to remove moisture and then at 210°C for 12 h to carry out the dehydration:

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O$$

The relative stabilities, with respect to loss of sulphur trioxide, of mixtures of vanadium pentoxide or sodium metavanadate with alkali metal sulphates and pyrosulphates were investigated by thermogravimetric analysis. To facilitate comparisons, 1 mmol of vanadium pentoxide, or 2 mmol of sodium metavanadate were always used, mixed with variable amounts of the other reagents (Table 1) and heated in a 10-ml vitreosil crucible on a Stanton TR1 thermobalance at a heating rate of 2 or 4°C min^{-1}. The weight losses are given as grams per mole of reagent (gpM), which numerically is identical to milligrams of weight loss per millimole of reagent. The physical appearance of some of these mixtures was observed by heating them under air up to 600°C at a rate of 2°C min^{-1} in a Quickfit pyrex test tube closed with a silica-gel drying tube. The percentage of vanadium present as vanadium(IV) in quenched samples was determined volumetrically with permanganate.

Infrared spectra of ground, solidified melt samples suspended in Nujol mulls between sodium chloride discs were obtained using a Unicam SP200 spectrometer.

RESULTS AND DISCUSSION

Firstly, the decomposition of pyrosulphate–sulphate, and vanadium pentoxide–sulphate mixtures will be described briefly for comparison with later results. The compositions of all mixtures used are given in Table 1.

Pyrosulphate–sulphate mixtures

Thermogravimetric analysis of alkali metal pyrosulphate–sulphate mixtures with varied proportions of lithium, sodium and potassium in binary and ternary combination are presented in Fig. 1. The destabilising influence of the smaller radii alkali metal cations on pyrosulphate is clearly evident, leading to weight losses at lower temperatures as sodium is substituted for potassium (e.g. Fig. 1, curves C vs. G, and D vs. E) and as lithium was introduced (e.g. curve A vs. F), which were undoubtedly due to the higher polarising power of the smaller cations, and it appears that this factor was dominant in the decomposition of pyrosulphate in the ternary sulphate eutectic (Fig. 1, curve B).

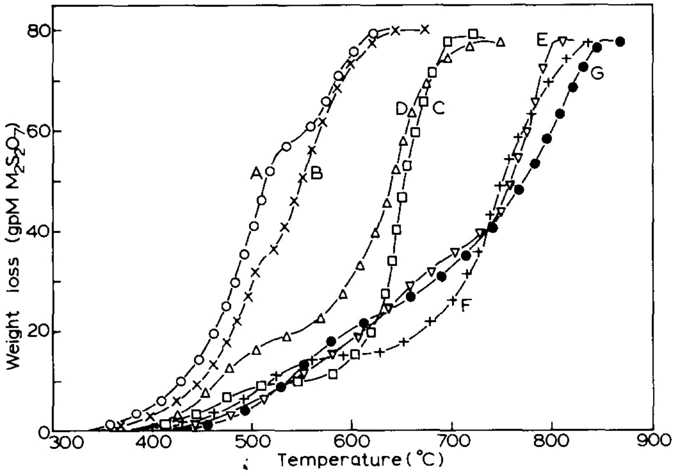

Fig. 1. Thermogravimetric analysis of alkali metal pyrosulphate in sulphate-containing melts (compositions in Table 1). Curve A (○): 1 mmol $K_2S_2O_7$, 2 mmol Li_2SO_4 (mixture 31). Curve B (×): 1 mmol $K_2S_2O_7$ in 2 g ternary eutectic (mixture 29). Curve C (□): 1 mmol $Na_2S_2O_7$, 2 mmol Na_2SO_4 (mixture 35). Curve D (△): 1 mmol $Na_2S_2O_7$ alone (mixture 34). Curve E (▽): 1 mmol $K_2S_2O_7$ alone (mixture 30). Curve F (+): 1 mmol $K_2S_2O_7$, 2 mmol Na_2SO_4 (mixture 32). Curve G (●): 1 mmol $K_2S_2O_7$, 10 mmol K_2SO_4 (mixture 33).

The influence of sulphate on the decomposition of pyrosulphate was less clear as the physical state of the mixtures changed considerably during weight loss. The alkali metal pyrosulphates melt around 400 °C forming a molten phase that will dissolve some of the sulphate [17]. While mixtures containing lithium sulphate formed low melting point sulphate systems that melted during decomposition, all the other mixtures became solid after decomposition was complete. At higher temperatures, mixture 32 ($K_2S_2O_7$: Na_2SO_4, Fig. 1, curve F) became very viscous when solution of sulphate was complete, while the all-sodium mixtures 34 and 35 (Fig. 1, curves D and C) also formed crusts and the rate of decomposition was greatly reduced by such physical barriers. The step in curve B ($K_2S_2O_7$ in eutectic), a temporary thermal arrest at the melting point (512 °C) of the bulk of this mixture, was probably due to the sudden reduction in gas/sulphate contact area when the eutectic melted.

In all cases decomposition of pyrosulphate was eventually complete, the weight loss being 79 ± 2 gpM, corresponding to the calculated loss of 80 gpM for the reaction:

$$M_2S_2O_7 \rightarrow M_2SO_4 + SO_3 \qquad (1)$$

Vanadium pentoxide–alkali metal sulphate

The results of heating equimolar mixtures of alkali metal sulphate with vanadium pentoxide are presented in Fig. 2 and in Table 1. These decompositions were not taken to completion, i.e. to a loss of 80 gpM of sulphur trioxide and total formation of a metavanadate, because at the very high temperatures necessary the reagents also attacked the vitreosil crucible.

$$M_2SO_4 + V_2O_5 \rightarrow 2MVO_3 + SO_3 \qquad (2)$$

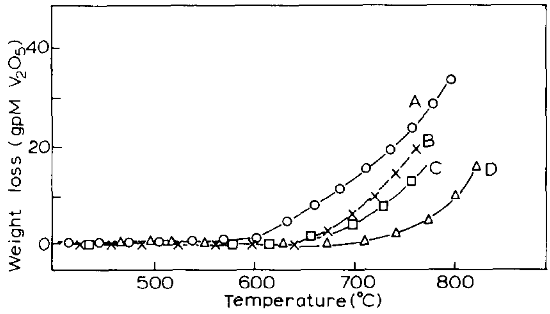

Fig. 2. Thermogravimetric analysis of vanadium pentoxide in sulphate melts (compositions in Table 1). Curve A (○): 1 mmol V_2O_5, 1 mmol Li_2SO_4 (mixture 1). Curve B (×): 1 mmol V_2O_5, 1 mmol Na_2SO_4 (mixture 2). Curve C (□): 1 mmol V_2O_5, 1 mmol K_2SO_4 (mixture 3). Curve D (△): 1 mmol V_2O_5, 2 g ternary eutectic (mixture 20).

The rapid 2 gpM loss from the sodium sulphate and ternary sulphate eutectic mixtures at 520 and 480 °C (Fig. 2, curves B and D, respectively), the slow loss of 3 gpM from the potassium sulphate mixture between 350 and 500 °C (curve C), and the initial slow loss from 400 °C from lithium sulphate (curve A) all probably represent vanadium bronze formation [18], oxygen being lost in the solid state. Notionally this is regained on fusion, although such a gain was only observed for the ternary sulphate eutectic (curve D). Weight losses at higher temperatures were due to sulphur trioxide evolution, as eqn. (2). Formation of metavanadate has been reported in a sodium sulphate–vanadium pentoxide (2 : 1 mole ratio) mixture heated to 900 °C [19].

Equimolar vanadium pentoxide–pyrosulphate with and without additional sulphate

The temperature of onset of discernible weight loss listed in Table 1, and the rate of decomposition (loss of sulphur trioxide) of vanadium pentoxide, alkali metal pyrosulphate/sulphate mixtures were both found to vary with the composition of the system. Equimolar mixtures of potassium pyrosulphate or sodium pyrosulphate with vanadium pentoxide but without additional sulphate (Fig. 3, curves A and B) started to decompose from 300 and 340 °C, respectively, but thereafter gave very similar weight loss curves, and were more stable than sodium pyrosulphate heated alone (Fig. 1, curve D) but less stable than potassium pyrosulphate heated alone (Fig. 1, curve E).

Addition of small quantities of potassium sulphate or sodium sulphate greatly stabilised the equimolar mixture, for example Fig. 3, curve K ($V_2O_5 : K_2S_2O_7 : K_2SO_4$, 1 : 1 : 2) where loss of sulphur trioxide only became discernible at 560 °C (as compared to loss at 300 °C, curve B). Potassium sulphate was consistently slightly more stabilising than sodium sulphate. Although addition of 2 mmol of lithium sulphate (Fig. 3, curve C) produced little stabilisation of the system, addition of the ternary sulphate eutectic (Fig. 4, curve E) (i.e. 2 g eutectic containing Li_2SO_4, 13.08 mmol; Na_2SO_4, 1.42 mM; K_2SO_4, 2.22 mM) delayed decomposition until 570 °C, and 2 g of the binary eutectic (Li_2SO_4, 10.37 mM; Na_2SO_4, 6.01 mM) had a similarly stabilising effect.

However, prolonged heating of a mixture of composition 1 : 1.33 $V_2O_5 : K_2S_2O_7$ in 2.0 g of ternary sulphate eutectic at 550 °C gave a loss of 0.45 mmol of sulphur trioxide after 17 h, at which point the system was still losing sulphur trioxide at a rate of 0.006 mM h^{-1}, indicating that the decomposition temperature of 570 °C (Fig. 4, curve E) for the equimolar mixture in the eutectic was affected by the rate of temperature rise as expected. Below the decomposition temperature most mixtures were viscous enough to contain gas bubbles which were trapped and not readily evolved.

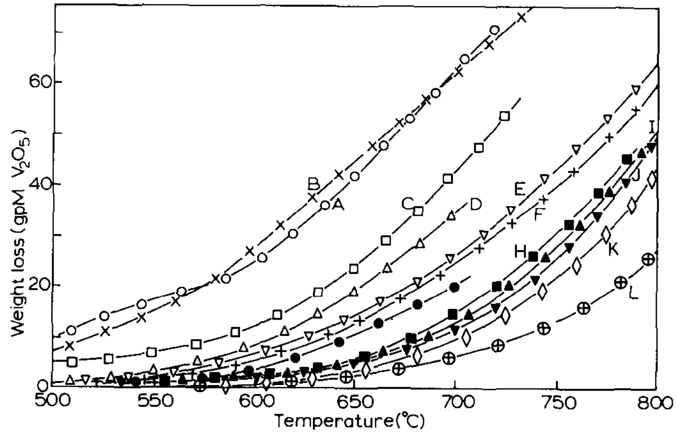

Fig. 3. Thermogravimetric analysis of equimolar vanadium pentoxide–pyrosulphate, with and without additional sulphate (compositions in Table 1). Curve A (○): 1 mmol V_2O_5, 1 mmol $Na_2S_2O_7$ (mixture 13). Curve B (×): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$ (mixture 4). Curve C (□): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 2 mmol Li_2SO_4 (mixture 11). Curve D (△): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, $\frac{1}{2}$ mmol K_2SO_4 (mixture 5). Curve E (▽): 1 mmol V_2O_5, 1 mmol $Na_2S_2O_7$, 1 mmol Na_2SO_4 (mixture 14). Curve F (+): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 1 mmol Na_2SO_4 (mixture 9). Curve G (●): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 1 mmol K_2SO_4 (mixture 6). Curve H (■): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, $\frac{1}{2}$ mmol Li_2SO_4, $\frac{3}{2}$ mmol K_2SO_4 (mixture 12). Curve I (▲): 1 mmol V_2O_5, 1 mmol Na_2SO_7, 2 mmol Na_2SO_4 (mixture 15). Curve J (▼): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 2 mmol Na_2SO_4 (mixture 10). Curve K (◇): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 2 mmol K_2SO_4 (mixture 7). Curve L (⊕): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 4 mmol K_2SO_4 (mixture 8).

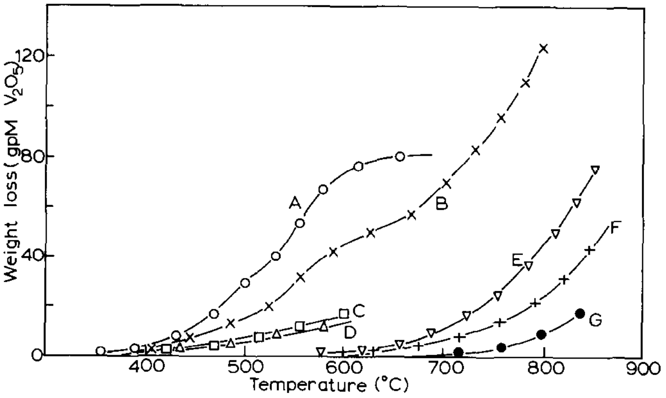

Fig. 4. Thermogravimetric analysis of vanadium pentoxide–pyrosulphate of various ratios in ternary sulphate eutectic (2 g). Curve A (○): 1 mmol $K_2S_2O_7$ (mixture 29). Curve B (×): 1 mmol V_2O_5, 2 mmol $K_2S_2O_7$ (mixture 27). Curve C (□): 1 mmol V_2O_5, $1\frac{1}{2}$ mmol $K_2S_2O_7$ (mixture 26). Curve D (△): 1 mmol V_2O_5, $\frac{4}{3}$ mmol $K_2S_2O_7$ (mixture 25). Curve E (▽): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$ (mixture 23). Curve F (+): 1 mmol V_2O_5, $\frac{1}{2}$ mmol $K_2S_2O_7$ (mixture 22). Curve G (●): 1 mmol V_2O_5 (mixture 20).

TABLE 2

Percentage reduction [V(IV)/V_{total} × 100] found in quenched samples (%)

Mixture	Composition	Temperature (°C)				
		400	450	500	550	600
4	$V_2O_5:K_2S_2O_7$, 1:1		10		12	
6	$V_2O_5:K_2S_2O_7:K_2SO_4$, 1:1:1			3.8		4.9
7	$V_2O_5:K_2S_2O_7:K_2SO_4$, 1:1:2	3.3		2.8		2.7
10	$V_2O_5:K_2S_2O_7:Na_2SO_4$, 1:1:2			4.3		5.8
15	$V_2O_5:Na_2S_2O_7:Na_2SO_4$, 1:1:2					7.8

To compliment the thermogravimetric results, the general appearance of some mixtures of vanadium pentoxide and alkali metal pyrosulphate was noted as they were heated in air at a rate of 2°C min^{-1}. Table 2 shows that vanadium was partially reduced to vanadium(IV) in quenched samples taken from these mixtures. Some components of the mixtures were observed to begin to melt between 300 and 350°C, but by 400°C exceedingly viscous, very darkly coloured, incompletely melted fluids had formed. As the temperature rose, mobility increased greatly, although gas bubbles when formed were trapped in the fluid and still not readily evolved. Addition of potassium sulphate or sodium sulphate had the effect of decreasing the percentage reduction with respect to the equimolar mixture (Table 2), and of increasing mobility and degree of fusion, the effect of potassium sulphate being the greater. By 600°C the equimolar mixture with potassium sulphate ($V_2O_5:K_2S_2O_7:K_2SO_4$, 1:1:2, mixture 7) was mobile and completely fluid but had lost little sulphur trioxide (Fig. 3, curve K) and had a low vanadium(IV) content. The quenched sample taken from this most homogeneous melt was used for infrared analysis (Fig. 5), discussed at the end of this section. Addition of 2.0 g of the ternary sulphate eutectic (mixture 23) also produced a mobile and well-mixed system.

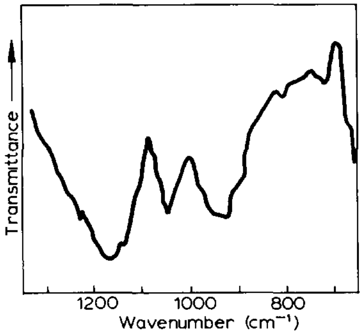

Fig. 5. Infrared spectrum of solidified mixture 7 (1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 2 mmol K_2SO_4) after thermogravimetric analysis to 600°C.

Finally it is noted that on cooling and solidification, mixture 15 (all sodium) evolved a gas, probably oxygen, indicating some vanadium bronze formation and hence production of vanadium(IV) at this point. The thermogravimetric samples also lost oxygen on solidification. However, for those mixtures heated to 800 °C less than 1% reduction to vanadium(IV) was found after cooling except for the "all-sodium" mixtures, where a maximum of 2.5% reduction was found.

There are few comparable results in the literature; however, Basarova et al. [4] also found equimolar vanadium pentoxide and potassium pyrosulphate to be partially reduced to vanadium(IV) and to be less stable than potassium pyrosulphate heated alone, giving values of 9.5% reduction at 550 °C and a weight loss of 16 gpM at 600 °C. These figures compare with 12% reduction and a weight loss of 27 gpM found in the present work at comparable temperatures. The high viscosity of vanadium pentoxide–potassium pyrosulphate mixtures below 450 °C has also been noted previously [20] with the suggestion that this may be due to polymerisation, a well-known feature of aqueous vanadium chemistry [13].

An exothermic effect at 275 °C during investigation of the vanadium pentoxide–potassium pyrosulphate phase diagram has been interpreted as the formation of a 1 : 1 or 1 : 1.25 compound [3,4]. The similarity of curves A and B (Fig. 3) indicates that a similar interaction may occur with sodium pyrosulphate. The stability of the equimolar mixture in the presence of added potassium sulphate or sodium sulphate suggests that there was little free pyrosulphate present. This implies interaction between vanadium pentoxide and pyrosulphate and probably also with sulphate to form vanado-sulphato polymer(s), possibly analogous to those recently identified by the Bjerrum [9,12] and Glazyrin [7,8,10,11] laboratories.

The alternative hypothesis of a simple Lux–Flood acid–base reaction of vanadium pentoxide, for example:

$$V_2O_5 + S_2O_7^{2-} \rightarrow 2VO_2^{+} + 2SO_4^{2-}$$

with the dioxovanadium(V) cations complexed by sulphate ligands is less attractive, in view of the well-established tendency of vanadium to polymerise and the viscous nature of the melts, and the observation that stabilisation continued to increase at least to effective VO_2^{2+}/SO_4^{2-} ratios of 1 : 6 (Fig. 3, curve L).

Lithium sulphate stabilised the system only slightly. This was probably due to polarisation effects on the postulated polynuclear anion, since Flood and Forland [21] have shown that the greater the polarising power of a cation, the greater is its destabilising effect on a large anion. Hence the system would be expected to lose sulphur trioxide fastest in the presence of highly polarising lithium ions, which was the case. However, in the presence of the ternary sulphate eutectic, the lower stabilising effect of lithium ions was apparently offset, presumably by the potassium and sodium sulphate contents, which suggests close association between the vanadium species and potassium or sodium cations. This was in contrast to the influence of lithium on pyrosulphate decomposition in the ternary sulphate eutectic (Fig. 1, curve B) where potassium had only a small stabilising effect (cf. Fig. 1, curves E and G).

The complexity of the infrared spectrum of the solidified sample from mixture 7 is typical for this system [4,22,23]. In this spectrum (Fig. 5) it is noteworthy that the strong bands at 1295 and 1250 cm^{-1} due to potassium pyrosulphate [4,24], the V=O stretch at 1030 cm^{-1} of vanadium pentoxide and the very broad band centred at 1120 cm^{-1} due to the ν_3 band of potassium sulphate [25] are no longer prominent, probably indicating complexation. When sulphate is a separate ligand having C_{3v} or C_{2v} symmetry it is known that the asymmetric S–O stretch, ν_3, is split into absorptions at approximately 1040 and 1130 cm^{-1}, or at 1050, 1105 and 1170 cm^{-1}, respectively, and ν_1 becomes infrared-active at 970–990 cm^{-1} [26]. However, the broad 950 cm^{-1} band probably indicates the presence of the very stable V=O bond of vanadium(V) compounds, which usually cause strong absorption between 900 and 1050 cm^{-1} [27]. More specifically the coordinated dioxovanadium(V) cation (VO_2^+) could be present since it absorbs at 917 and 865 cm^{-1} in oxalato and at 920 and 883 cm^{-1} in fluoro complexes [28] and possibly at 940 and 913 cm^{-1} in water [29], while absorptions between 750 and 900 cm^{-1} may be due to V–O–V or S–O–S groups [24]. Finally it should be noted that there may also be some small absorption due to pyrosulphate [30].

Vanadium pentoxide–potassium pyrosulphate (1 : 2 molar ratio)

Vanadium pentoxide and potassium pyrosulphate in the ratio 1 : 2 decomposed from 300 ° C (i.e. mixture 16, Fig. 6, curve A) and lost sulphur trioxide considerably more rapidly than the equimolar mixture (mixture 4, Fig. 6, curve B) indicating that the latter reactant ratio led to more stable polymers. Again potassium sulphate gave additional stability to the system, which increased both with the amount of sulphate (cf. mixtures 16, 17 and 18, Fig. 6, curves, A, C and D, respectively) and with decreasing pyrosulphate (cf. Fig. 6, curves C and E). In fact mixture 17 ($V_2O_5 : K_2S_2O_7 : K_2SO_4$, 1 : 2 : 2; Fig. 6, curve C) was only slightly less stable than potassium pyrosulphate heated alone (Fig. 1, curve E; i.e. it was close to a 1 : 1 : 2, $V_2O_5 : K_2S_2O_7 : K_2SO_4$ mixture, with 1 mmol $K_2S_2O_7$ decomposing freely), that is, the destabilising effect of vanadium pentoxide on pyrosulphate had been almost completely nullified. Once again melt viscosity may have had some influence, since the even more stable mixture 18 (Fig. 6, curve D) was also very viscous (i.e. though fluid it would not pour at 800 ° C). In contrast the addition of much more sulphate as ternary eutectic (2 g, being a total of 16.6 mmol, Fig. 4, curve B) produced a mobile melt, which was only a little more

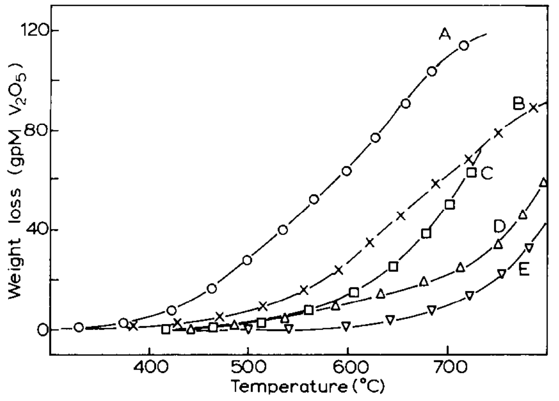

Fig. 6. Thermogravimetric analysis of vanadium pentoxide–pyrosulphate with and without additional sulphate. Curve A (○): 1 mmol V_2O_5, 2 mmol $K_2S_2O_7$ (mixture 16). Curve B (×): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$ (mixture 4). Curve C (□): 1 mmol V_2O_5, 2 mmol $K_2S_2O_7$, 2 mmol K_2SO_4 (mixture 17). Curve D (△): 1 mmol V_2O_5, 2 mmol $K_2S_2O_7$, 4 mmol K_2SO_4 (mixture 18). Curve E (▽): 1 mmol V_2O_5, 1 mmol $K_2S_2O_7$, 2 mmol K_2SO_4 (mixture 7).

stable than potassium pyrosulphate in the eutectic (Fig. 4, curve A), progressive increase in the proportion of vanadium pentoxide showing a steady increase in stability (Fig. 4, curves B, C and D from mixtures 27, 26 and 25), although all began to lose some weight from 340 °C, the decomposition temperature of potassium pyrosulphate in the ternary eutectic.

Sodium metavanadate and sodium orthovanadate with potassium pyrosulphate

Mixtures of sodium metavanadate and potassium pyrosulphate with 2 g of the ternary sulphate eutectic gave weight loss curves which were very similar to those obtained with equivalent amounts of vanadium pentoxide, i.e. the decomposition curve of mixture 21 of mole ratio $NaVO_3 : K_2S_2O_7$, 2 : 1 (Fig. 7, curve D), was similar to that of vanadium pentoxide heated with the eutectic (Fig. 4, curve G), suggesting that a Lux–Flood acid–base reaction occurs i.e.

$$2NaVO_3 + K_2S_2O_7 \rightarrow V_2O_5 + Na_2SO_4 + K_2SO_4$$

Similarly mixtures 24 and 28 ($NaVO_3 : K_2S_2O_7$ ratios of 2 : 2 and 2 : 3, respectively) gave weight losses (Fig. 7, curves C and B) which closely parallelled those of mixtures 23 and 27 (Fig. 4, curves E and B, $V_2O_5 : K_2S_2O_7$ ratios 1 : 1 and 1 : 2). Thus it appears that metavanadate had reacted with pyrosulphate at temperatures below its temperature of decomposition. Sodium metavanadate alone was stable in the ternary eutectic to above 900 °C [14].

In contrast, sulphur trioxide was lost freely from sodium orthovanadate–

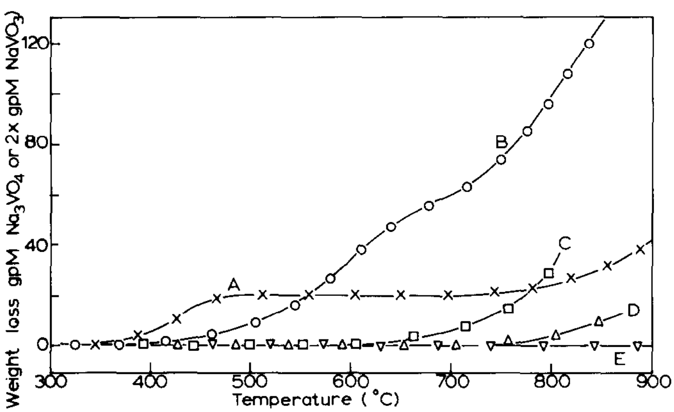

Fig. 7. Thermogravimetric analysis of sodium orthovanadate and metavanadate–pyrosulphate of various ratios in ternary sulphate eutectic (2 g). Curve A (×): 1.01 mmol Na_3VO_4, 1.77 mmol $K_2S_2O_7$ (mixture 36). Curve B (○): 2 mmol $NaVO_3$, 3 mmol $K_2S_2O_7$ (mixture 28). Curve C (□): 2 mmol $NaVO_3$, 2 mmol $K_2S_2O_7$ (mixture 24). Curve D (△): 2 mmol $NaVO_3$, 1 mmol $K_2S_2O_7$ (mixture 21). Curve E (▽): $NaVO_3$ alone.

potassium pyrosulphate/ternary sulphate eutectic mixtures up to 450 °C (Fig. 7, curve A), when weight loss slowed and almost ceased at 480 °C. The temperature of any further weight losses then depended on the mole ratio of reagents remaining. For example mixture 36 of initial composition 1.01 mmol Na_3VO_4, 1.77 mM $K_2S_2O_7$ in 2.0 g of eutectic lost 20 mg (0.25 mM SO_3) between 340 and 480 °C and then remained at constant weight until 670 °C, when weight loss began again, i.e. $1.77 - 0.25 = 1.52$ mM of potassium pyrosulphate were available to react with 1.01 mM of sodium orthovanadate, a ratio of 3 : 2, and the following stoichometry may be envisaged:

$$2Na_3VO_4 + 3K_2S_2O_7 \rightarrow V_2O_5 + 3K_2SO_4 + 3Na_2SO_4$$

The temperature at which weight loss recommenced (~670 °C) was consistent with that obtained for mixture 20 (1 mmol V_2O_5 in 2 g ternary eutectic, Fig. 2, curve D) and for mixture 21 ($NaVO_3 : K_2S_2O_7$ ratio = 2 : 1, Fig. 4, curve H), indicating that the additional sodium and potassium sulphate formed in these Lux–Flood acid–base reactions had little effect in the presence of much lithium sulphate from the ternary eutectic.

The unexpected higher reaction temperature for the ostensibly more basic orthovanadate may imply that sodium orthovanadate does not dissolve in the molten pyrosulphate phase, or may be due to the different nature of the vanadates, since sodium orthovanadate is composed of discrete ions in a lattice, while both vanadium pentoxide and sodium metavanadate have polymeric structures with holes [31] which may allow penetration and more ready reaction of pyrosulphate.

CONCLUSION

The general trend found here, that the rate of loss of sulphur trioxide from vanadium pentoxide–pyrosulphate mixtures was greatly reduced by the addition of potassium sulphate or sodium sulphate, may in part account for the observation by Kato et al. [23] that above 500 °C loss of sulphur trioxide becomes the rate-determining step in the contact-catalysed oxidation of sulphur dioxide, since as the temperature is raised the concentration of sulphur trioxide (as $S_2O_7^{2-}$) in the liquid phase of the catalyst increasingly falls below that which is stoichiometrically necessary for all the alkali metal to be present as pyrosulphate [32], implying increasing concentration of sulphate. The stabilisation found was not principally a result of the effect of added sulphate on the equilibrium:

$$S_2O_7^{2-} \rightleftharpoons SO_4^{2-} + SO_3$$

but was consequent on interaction between vanadium pentoxide, pyrosulphate and sulphate and was most marked for equimolar ratios of vanadium pentoxide and pyrosulphate.

ACKNOWLEDGEMENTS

Thanks are extended to ISC Chemicals Ltd. and to the SERC for their CASE award to R.I.D.

REFERENCES

1 V.V. Illarianov, R.P. Ozerov and E.V. Kil'disheva, Russ. J. Inorg. Chem., 2 (1957) 883.
2 V.S. Haele and A. Meisel, Z. Anorg. Chem., 375 (1970) 24.
3 V.S. Haele and A. Meisel, Kinet. Katal., 12 (1971) 1276.
4 Zh.G. Basarova, G.K. Boreskov, L.M. Kefeli, L.G. Karakchiev and A.A. Ostan'kovich, Dokl. Akad. Nauk., USSR, 180 (1968) 421.
5 S. Weychert and A. Urbanck, Int. Chem. Eng., 9 (1969) 396.
6 C.N. Kenney, Catalysis, 3 (1980) 123.
7 M.P. Glazyrin, V.N. Krasilnikov and A.A. Ivakin, Russ. J. Inorg. Chem., 25 (1980) 1843.
8 M.P. Glazyrin, V.N. Krasilnikov and A.A. Ivakin, Russ. J. Inorg. Chem., 26 (1981) 1436.
9 N.H. Hansen, R. Fehrmann and N.J. Bjerrum, Inorg. Chem., 21 (1982) 744.
10 V.N. Krasilnikov and M.P. Glazyrin, Russ. J. Inorg. Chem., 27 (1982) 1506.
11 M.P. Glazyrin, V.N. Krasilnikov and A.A. Ivakin, Russ. J. Inorg. Chem., 29 (1984) 1783.
12 R. Fehrmann, B. Krebs, G.N. Papatheodorou, R.W. Berg and N.J. Bjerrum, Inorg. Chem., 25 (1986) 1571.
13 M.T. Pope and B.W. Dale, Q. Rev. Chem. Soc., 22 (1968) 527.
14 R.I. Dearnaley and D.H. Kerridge, Thermochim. Acta, 63 (1983) 219.
15 E.K. Akopov and A.G. Bergman, Russ. J. Inorg. Chem., 4 (1959) 520.
16 R.I. Dearnaley, D.H. Kerridge and D.J. Rogers, Inorg. Chem., 22 (1983) 3242.

17 L.P. Kostin, N.L. Chikishev, A.N. Ketov and V.V. Pechkovski, Izv. Vyssh. Ucheb. Zaveb., Khim. Khim. Tekhnol., 14 (1971) 1787.

18 A.A. Fotiev, Russ. J. Inorg. Chem., 14 (1969) 645.

19 A.A. Fotiev and B.V. Slobodin, Russ. J. Inorg. Chem., 10 (1965) 80.

20 S.V. Ivanenko, N.S. Totochesnikov and V.P. Saltanova, Zh. Vses. Khim. Obsh., 17 (1972) 110.

21 H. Flood and T. Forland, Acta Chem. Scand., 1 (1947) 592, 781.

22 Zh.G. Bazarova, G.K. Boreskov, A.A. Ivanov, L.G. Karakchiev and L.D. Kochkena, Kinet. Katal., 12 (1971) 949.

23 A. Kato, K. Tomoda, I. Mochida and T. Seiyama, Bull. Soc. Chem. Jpn., 45 (1972) 690.

24 G.E. Walrafen, D.E. Irish and T.F. Young, J. Chem. Phys., 37 (1962) 662.

25 R.A. Nyquist and R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York, 1971.

26 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1970.

27 J. Selbin, L.H. Holmes and S.P. McGlynn, J. Inorg. Nucl. Chem., 25 (1963) 1359.

28 W.P. Griffith and T.D. Wickens, J. Chem. Soc. A, (1968) 400.

29 W.P. Griffith and P.J.B. Lesniak, J. Chem. Soc. A, (1969) 1066.

30 A. von Simon and H. Wagner, Z. Anorg. Chem., 311 (1961) 102.

31 A.F. Wells, Structural Inorganic Chemistry, 3rd edn., Oxford University Press, Oxford, 1962.

32 G.H. Tandy, J. Appl. Chem., 6 (1956) 68.