Thermochimica Acta, 42 (1980) 165—175
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

MOLTEN LITHIUM SULPHATE—SODIUM SULPHATE—POTASSIUM SULPHATE EUTECTIC. THE REACTIONS OF CONDENSED PHOSPHATES

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(Received 15 April 1980)

ABSTRACT

The reactions of several condensed phosphates in molten lithium sulphate—sodium sulphate—potassium sulphate eutectic have been studied. Tetrametaphosphate, trimetaphosphate, and both soluble and insoluble forms of metaphosphate degraded in three stages; the first stage produced tripolyphosphate and sulphur trioxide. Polymeric sulphatophosphate species, of various chain lengths, have been suggested as intermediates in the first stage reaction of these metaphosphates. Tripolyphosphate reacted in two steps, producing pyrophosphate and sulphur trioxide in the first step. Pyrophosphate reacted further to form orthophosphate and sulphur trioxide. Potassium orthophosphate was stable in the melt up to 1000°C. The stoichiometries of these reactions were established by thermogravimetric analysis.

INTRODUCTION

Molten salts containing oxyanions, such as molten sulphates, can be characterised as acid—base systems according to Lux [1] and Flood et al. [2—4]. In this concept, an oxide ion acceptor is an acid, while an oxide ion donor is a base.

In molten alkali metal sulphates, the sulphate ion dissociates [5] according to

$$2\ SO_4^{2-} \rightleftharpoons S_2O_7^{2-} + O^{2-} \quad (1)$$

and

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

The overall equilibrium can thus be represented as

$$SO_4^{2-} \rightleftharpoons SO_3 + O^{2-} \quad (3)$$

and

$$[O^{2-}] \times P_{SO_3} = \text{constant} \quad (4)$$

where P_{SO_3} is the partial pressure of sulphur trioxide in the atmosphere in equilibrium with the melt. Thus, when P_{SO_3} decreases, the melt starts to decompose slowly. Decomposition is also enhanced by the presence of an oxide ion acceptor, e.g. metaphosphate which degrades gradually into ortho-

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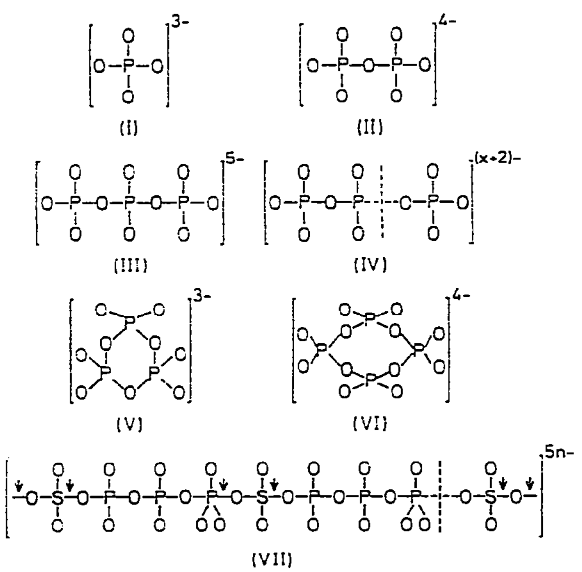


Fig. 1. Structural formulae. I, PO_4^{3-}(OP); II, $P_2O_7^{4-}$(PP); III, $P_3O_{10}^{5-}$(TPP); IV, $P_xO_{3x+1}^{(x+2)} \simeq (PO_3)_x^{x-}$(MP); V, $P_3O_9^{3-}$(TMP); VI, $P_4O_{12}^{4-}$(TTMP); VII, the polymeric sulphatophosphate species.

phosphate [5].

$$PO_3^- + SO_4^{2-} \rightarrow PO_4^{3-} + SO_3 \qquad (5)$$

The family of condensed phosphates represents an interesting series of Lux—Flood acids. Structural formulae of the phosphates studied in the present work are given in Fig. 1 (the symbols OP, PP, TPP, MP, TTMP, and TMP will be used as abbreviations). In all these species (I—VI), the phosphorus atoms attained their maximum coordination number of 4. Stoichiometrically, the only difference is their relative deficiency of oxide ions. This deficiency increases as one goes from species I to V, with VI having the same deficiency as V. Accordingly, their acid strength in a given base, such as molten sulphates, should be TTMP $\simeq$ TMP $\simeq$ MP > TPP > PP > OP.

Several studies on the depolymerisation reactions of condensed phosphates in molten salts have been reported. Shams El Din et al. [6—12] have studied the degradation of phosphorus pentoxide and metaphosphate and pyrophosphate ions in various molten salts. Potentiometric titration of sodium metaphosphate, dissolved in molten lithium chloride—potassium chloride eutectic at 400° C, with sodium peroxide was represented as

$$2\ PO_3^- + O^{2-} \rightarrow P_2O_7^{4-} \qquad (6)$$

with no further reaction to orthophosphate. In molten potassium nitrate, however, titration of sodium metaphosphate with sodium peroxide resulted in reaction (6) followed by

$$P_2O_7^{4-} + O^{2-} \rightarrow 2\ PO_4^{3-} \qquad (7)$$

Finally, when solutions of sodium metaphosphate in molten potassium nitrate at 350° C were titrated with weaker bases, such as carbonate or bicarbonate, the reaction proceeded according to the equations

$$3\ PO_3^- + O^{2-} \rightarrow P_3O_{10}^{5-} \qquad (8)$$

and

$$2\ P_3O_{10}^{5-} + O^{2-} \rightarrow 3\ P_2O_7^{4-} \qquad (9)$$

followed by reaction (7).

Copland and Gutierrez [13] reported that trimetaphosphate, tetrametaphosphate, metaphosphate $(PO_3)_x^{x-}$ and tripolyphosphate degraded to pyrophosphate in molten sodium nitrate at 450° C. In molten lithium nitrate at 420° C, however, the final product was found to be orthophosphate, a result which was attributed to cationic effect.

Kerridge and coworkers [14—16] have studied the degradation of various condensed phosphates in molten nitrates, nitrite, and carbonate. In all these melts, the final product was orthophosphate with pyrophosphate as an intermediate.

Markowitz et al. [17] have investigated the depolymerisation of alkali metal phosphates with their corresponding perchlorates. The degradation of these phosphates, which was found to depend on the associated cation, can be represented by the equation

$$2\ MPO_3 + 2\ MClO_4 \rightarrow M_4P_2O_7 + Cl_2 + \tfrac{1}{2}\ O_2 \qquad (10)$$

and further, if M = Li

$$M_4P_2O_7 + 2\ MClO_4 \rightarrow 2\ M_3PO_4 + Cl_2 + \tfrac{1}{2}\ O_2 \qquad (11)$$

In contrast, no detailed study of the behaviour of the condensed phosphates in molten sulphate has been reported. Thus, in the present work, a systematic investigation of the chemistry of these phosphates in molten lithium sulphate—sodium sulphate—potassium sulphate eutectic was carried out and the stoichiometries of their reactions were established using thermogravimetric analysis.

EXPERIMENTAL

Materials

Reagent grade soluble sodium metaphosphate (Riedel-de Haen) and insoluble sodium metaphosphate (B.D.H.) were dried at 120° C for 20 h. Reagent grade potassium orthophosphate (B.D.H.) and sodium tetrametaphosphate (Albright and Wilson) were dried at 220°C for 6 h and at 150°C for 20 h, respectively. Reagent grade anhydrous sodium pyrophosphate (B.D.H.) was used as received.

Sodium tripolyphosphate (Alfa product) was purified by recrystallisation four times from 30% ethanol [18]. Sodium trimetaphosphate was prepared by heating a mixture of 30 g Analar disodium hydrogen orthophosphate dihydrate (Merck) and 17 g Analar ammonium nitrate (B.D.H.) for 6 h at

TABLE 1

R_F values of some phosphates

Compound	R_F value
K_3PO_4	0.78
$Na_4P_2O_7$	0.60
$Na_5P_3O_{10}$	0.47
$Na_3(PO_3)_3$	0.35
$Na_4(PO_3)_4$	0.27

310—320° C. The white crystalline product was dissolved in water, filtered, and allowed to crystallise. The anhydrous salt was obtained by extended storage above 20° C [19].

Analar lithium sulphate (B.D.H.), sodium sulphate (Hopkin and Williams), and potassium sulphate (Riedel-de Haen) were dried at 200° C for 2 h, cooled in a desiccator, mixed in the eutectic ratio (78 : 13.5 : 8.5 mole%) [20], melted, solidified, finely ground, and stored in a dry box.

Analysis

Reacted melt solutions were solidified, dissolved in water and qualitatively analysed for phosphates by paper chromatography [18] using Whatman No. 1 papers as the stationary phase. The mobile phase was prepared by dissolving 25 g trichloroacetic acid in a mixture of 625 ml isopropanol, 125 ml isobutanol, 7.5 ml ammonia solution (s.g. = 0.88) and 250 ml of distilled water. The spray reagent was prepared by addition of 5 ml of 60% perchloric acid, 1 ml of conc. hydrochloric acid (s.g. = 1.18), and 1 g of ammonium molybdate to enough distilled water to make 100 ml of solution. The R_F values obtained from paper chromatography of some phosphate compounds, with a solvent front of about 12—13 cm, are listed in Table 1.

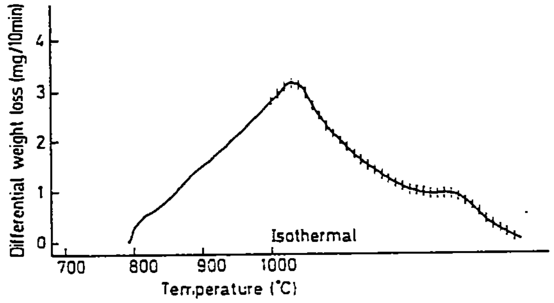
Procedure

Reactions were carried out using 1 or 2 g of the reactant mixture in 5 or 10 ml alumina crucibles, respectively, on a Stanton Redcroft MF-H5 mass flow thermobalance with a heating rate of 2° C min^{-1} under a nitrogen atmosphere. Differential thermal analyses were carried out using 0.2 g of the reactant mixture on a MOM Q-Derivatograph with a heating rate of 10° C min^{-1} in air. All reactants were ground to a fine powder and very well mixed.

Infrared spectra were taken of powdered samples pressed into thin discs with potassium bromide on a Perkin-Elmer 377 spectrometer.

RESULTS AND DISCUSSION

Potassium orthophosphate was moderately soluble in the molten sulphate eutectic. Its solutions were stable up to 1000°C, but above this temperature



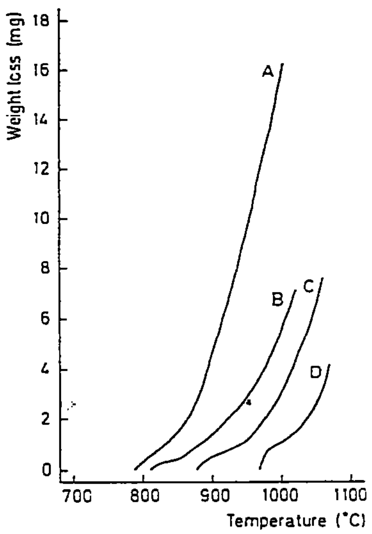


Fig. 2. Thermogravimetry of 0.59 m $Na_4P_2O_7$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

Fig. 3. Thermogravimetry of $Na_4P_2O_7$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic. A, 0.59 m; B, 0.90 m; C, 1.22 m; D, 3.70 m.

commenced to lose weight steadily as sulphur trioxide started to evolve due to the decomposition of the melt.

Sodium pyrophosphate, which was soluble in the molten sulphate eutectic, reacted at 790°C evolving sulphur trioxide. The final product was identified as orthophosphate by paper chromatography ($R_F = 0.78$) and by a qualitative test with silver nitrate [18]. Thermogravimetric analysis (Fig. 2) showed a one-stage reaction with an average total weight loss of 30.4% corresponding to the reaction

$$P_2O_7^{4-} + SO_4^{2-} \rightarrow 2\,PO_4^{3-} + SO_3 \qquad (12)$$

(Calculated for loss of 1 S + 3 O per $Na_4P_2O_7$ = 30.1%).

Thermogravimetric analysis (Fig. 3) also showed that the initial reaction temperature is dependent on the molal concentration of sodium pyrophosphate in the melt. This dependence was attributed to the availability of lithium ions in the nearest surroundings of the pyrophosphate; as the concentration of the latter increases, the availability of the former decreases. The small, highly polarising lithium ion probably has a weakening effect on the P—O—P bridge bond, which is then more easily attacked by oxide ions present in equilibrium with the sulphate melt [eqn. (3)]. Changes in the sodium pyrophosphate crystal structure with temperature, shown by differential thermal analysis [21], did not affect the course of the reaction.

Sodium tripolyphosphate is thermally unstable at 622°C, undergoing the reversible reaction [22]

$$Na_5P_3O_{10} \xrightarrow{622^\circ C} NaPO_3 + Na_4P_2O_7 \qquad (13)$$

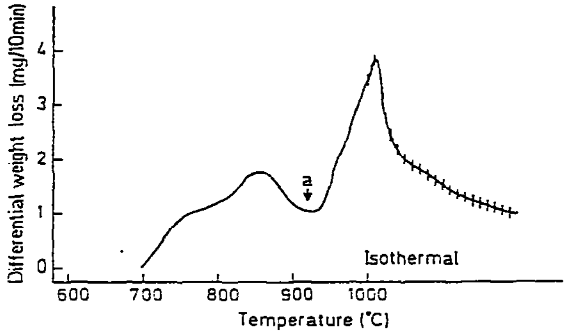


Fig. 4. Thermogravimetry of 0.69 m $Na_5P_3O_{10}$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

In the molten sulphate eutectic, however, this reaction was found to be irreversible. This was shown by paper chromatography of the solidified melt solutions which revealed two spots, one with an R_F value of 0—0.42, which was assigned to various metaphosphates of different molecular weights and the other with an R_F value of 0.60, which was pyrophosphate. Moreover, the irreversibility of the reaction was found to be dependent on the concentration of the tripolyphosphate since at higher concentrations (>0.5 m) paper chromatography of the solidified melts revealed a spot with an R_F value of 0.47, indicating the presence of tripolyphosphate. Thus, the melt is probably acting as a barrier between the two products, thereby hindering the reverse reaction. Thermogravimetric analysis (Fig. 4) showed that the tripolyphosphate reaction with the melt occurs in two stages, the first commencing at 700° C with a maximum rate at 840° C, and the second with a maximum rate around 1000° C. The loss at the end of the first stage, marked by an arrow (a) averaged 13.3%, not too far from that expected from the formation of pyrophosphate.

$$2\ P_3O_{10}^{5-} + SO_4^{2-} \rightarrow 3\ P_2O_7^{4-} + SO_3 \qquad (14)$$

(Calculated for loss of $\frac{1}{2}$ S + $\frac{3}{2}$ O per $Na_5P_3O_{10}$ = 10.9%). The overall weight loss was 52.3%, corresponding to the equation

$$P_3O_{10}^{5-} + 2\ SO_4^{2-} \rightarrow 3\ PO_4^{3-} + SO_3 \qquad (15)$$

(Calculated for loss of 1 S + 3 O per $Na_5P_3O_{10}$ = 52.3%). Qualitative analysis and paper chromatography (R_F = 0.78) of the final product indicated the presence of orthophosphate only. Thus, the tripolyphosphate reaction has probably proceeded via the initial formation of metaphosphate and pyrophosphate at 622° C followed by the reaction of metaphosphate to pyrophosphate at 700°C and eventually to orthophosphate.

Sodium tetrametaphosphate alone undergoes a structural change around 450° C to sodium trimetaphosphate [23]. This result was confirmed in the present work by differential thermal analysis (Fig. 5, curve A), which also shows a second endothermic peak at 620° C due to the melting of the product at this temperature. The product was identified, as sodium trimetaphosphate by a qualitative test with magnesia mixture [18], by paper chromato-

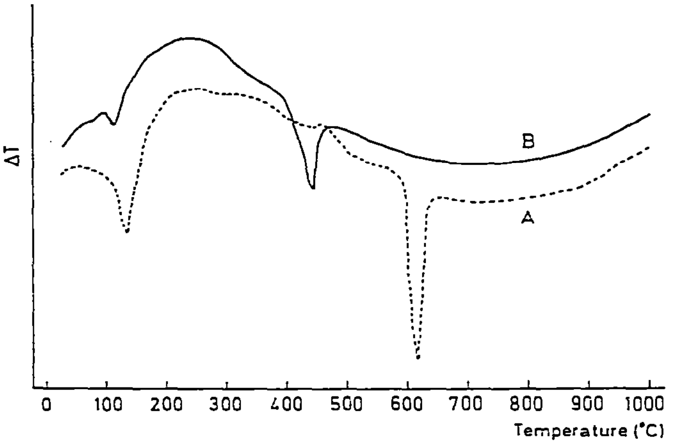


Fig. 5. Differential thermal analysis. A, $Na_4P_4O_{12}$; B, $Na_4P_4O_{12}$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

graphy ($R_F = 0.35$), and by its infrared bands at the following wave numbers: 685 (m), 765 (br, s), 985 (br, s), 1100 (s), 1290 (br, s) and 2915 (s) [18]. Mixtures of the sulphate eutectic (m.p. = 512°C) and sodium tetrametaphosphate melted at a lower temperature (at 450°C), which explains the marked endothermic effect shown by differential thermal analysis (Fig. 5, curve B) at this temperature. Paper chromatography of solidified melt solutions of tetrametaphosphate, after being kept at 450°C for 3 h, revealed a long spot with an R_F value of 0—0.47, indicating the presence of several unknown species, instead of trimetaphosphate. Attempts to separate these species were unsuccessful. At 500°C, tetrametaphosphate reacted with the melt evolving sulphur trioxide and after a reaction time of 3 h, analysis of solidified melts showed a tailing spot with an R_F value of 0—0.47. In addition to the unknown species, mentioned earlier, tripolyphosphate was suggested to be among the products of the reaction at this temperature, since its R_F value of 0.47 corresponds to one end of the tailing spot and its formation will explain the evolution of sulphur trioxide according to eqn. (16). Tripolyphosphate might also have been among the products of the reaction at 450°C since sulphur trioxide, though not observed, can be present in the melt, particularly at this relatively low temperature, as pyrosulphate according to equilibrium (3). At 700°C, the products of the reaction were tripolyphosphate and a very small amount of pyrophosphate, but the latter was the

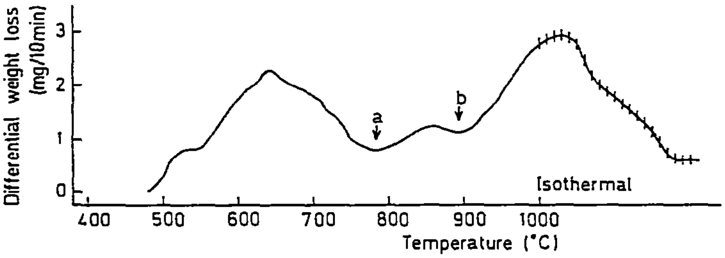


Fig. 6. Thermogravimetry of 0.12 m $Na_4P_4O_{12}$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

only product when the temperature increased further to 800° C. The final product, obtained at 1000° C, was orthophosphate. Thermogravimetric analysis (Fig. 6) showed three fairly separated stages of weight loss. The minima of the thermogram (arrows a and b), at 29.7 and 39.5%, were not far from those expected from the formation of tripolyphosphate and pyrophosphate, respectively, viz.

$$3\,P_4O_{12}^{4-} + SO_4^{2-} \rightarrow P_3O_{10}^{5-} + SO_3 \tag{16}$$

(Calculated for loss of 5/4 S + 4 O per $Na_4P_4O_{12}$ = 26.2%)

$$P_4O_{12}^{4-} + 2\,SO_4^{2-} \rightarrow 2\,P_2O_7^{4-} + 2\,SO_3 \tag{17}$$

(Calculated for loss of 2 S + 6 O per $Na_4P_4O_{12}$ = 39.3%). The overall loss averaged 78.9% which was close to that of the stoichiometry

$$P_4O_{12}^{4-} + 4\,SO_4^{2-} \rightarrow 4\,PO_4^{3-} + 4\,SO_3 \tag{18}$$

(Calculated for loss of 4 S + 12 O per $Na_4P_4O_{12}$ = 78.5%).

The reaction of tetrametaphosphate with the sulphate melt has thus proceeded through several stages. The most probable initial step is the thermal degradation of the tetrametaphosphate ring into smaller $P_3O_9^{3-}$ chains. It is suggested that this step is followed by polymerisation of these chains through sulphate bridging to form sulphatophosphate polymeric species (Fig. 1, species VII) of various lengths, instead of ring closing to form the trimetaphosphate expected from the thermal behaviour of the tetrametaphosphate alone. These two steps do not affect the stoichiometry of the reaction. The suggested sulphatophosphate polymeric species, being unstable at higher temperatures (~500° C), depolymerised by breaking the bonds marked by arrows to sulphur trioxide and tripolyphosphate, which reacted further to form pyrophosphate and eventually orthophosphate.

Sodium trimetaphosphate reacted with the melt in a manner similar to that of sodium tetrametaphosphate. Paper chromatography of the products at 450 and 500° C showed that trimetaphosphate had polymerised forming the same polymeric species (R_F = 0—0.47) as those obtained in the tetrametaphosphate reaction, which degraded to tripolyphosphate (at 600° C) and, at a higher temperature (700° C), to pyrophosphate. Thermogravimetric analysis (Fig. 7) showed three stages of weight loss commencing at 480° C. Analy-

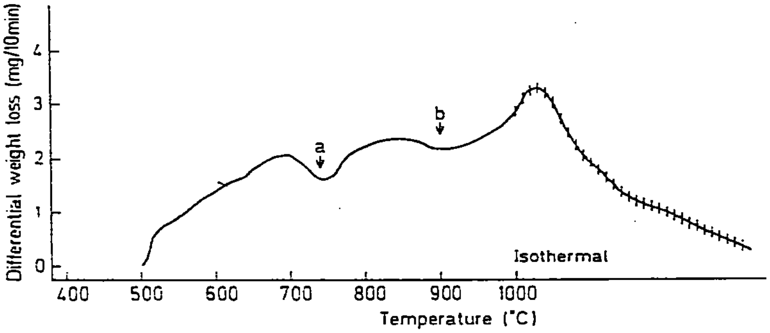


Fig. 7. Thermogravimetry of 0.08 m $Na_3P_3O_9$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

sis of the products at 1000°C indicated the presence of orthophosphate only. The losses at (a) and (b) averaged 25.7 and 43.9%, not far from those calculated for the formation of tripolyphosphate and pyrophosphate, respectively, viz.

$$P_3O_9^{3-} + SO_4^{2-} \rightarrow P_3O_{10}^{5-} + SO_3 \qquad (19)$$

(Calculated for loss of 1 S + 3 O per $Na_3P_3O_9$ = 26.2%)

$$2\ P_3O_9^{3-} + 3\ SO_4^{2-} \rightarrow 3\ P_2O_7^{4-} + 3\ SO_3 \qquad (20)$$

(Calculated for loss of $\frac{3}{2}$ S + $\frac{9}{2}$ O per $Na_3P_3O_9$ = 39.3%).

The overall loss averaged 78.0% which was close to that of the stoichiometry

$$P_3O_9^{3-} + 3\ SO_4^{2-} \rightarrow 3\ PO_4^{3-} + 3\ SO_3 \qquad (21)$$

(Calculated for loss of 3 S + 9 O per $Na_3P_3O_9$ = 78.5%).

Both soluble and insoluble forms of sodium metaphosphate reacted with the melt in a similar manner. Identification, by paper chromatography, of their reaction products at several temperatures (500, 600, and 700°C) showed a long tailed spot with an R_F value of 0—0.47, indicating the presence of the suggested sulphatophosphate species as well as tripolyphosphate. On leaving the reactions at 700°C for 3 h, paper chromatography revealed the presence of both tripolyphosphate and pyrophosphate. Thermogravimetric analyses of soluble and insoluble sodium metaphosphate (Figs. 8 and 9) showed three stages of weight loss commencing at 490 and 480°C, respectively. The arrow (a) in both thermograms indicated losses of 26.2 and 27.8%, respectively, close to that calculated for the formation of tripolyphosphate, viz.

$$3(PO_3)_x^{x-} + x\ SO_4^{2-} \rightarrow x\ P_3O_{10}^{5-} + x\ SO_3 \qquad (22)$$

(Calculated for loss of $x/3$ S + x O per $Na_x(PO_3)_x$ = 26.2%). At arrow (b), losses averaged 35.4 and 41.7%, respectively, not too far from that expected from the formation of pyrophosphate

$$2(PO_3)_x^{x-} + x\ SO_4^{2-} \rightarrow x\ P_2O_7^{4-} + x\ SO_3 \qquad (23)$$

(Calculated for loss of $x/2$ S + $3x/2$ O per $Na_x(PO_3)_x$ = 39.3%). The overall

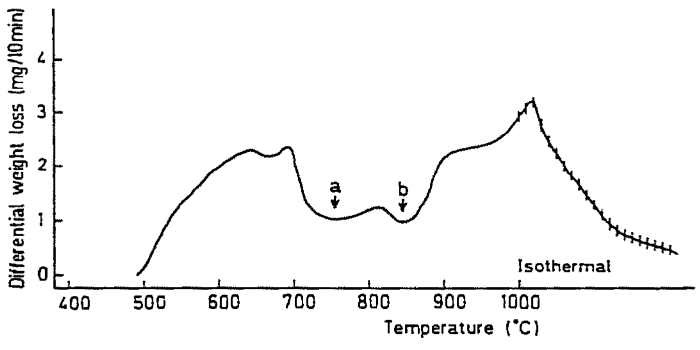


Fig. 8. Thermogravimetry of 0.06 m soluble $Na_x(PO_3)_x$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

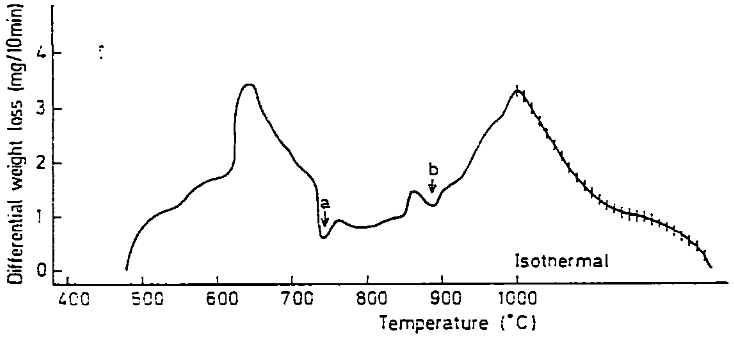


Fig. 9. Thermogravimetry of 0.05 m insoluble $Na_x(PO_3)_x$ in lithium sulphate—sodium sulphate—potassium sulphate eutectic.

losses averaged 78.6 and 79.2%, respectively, which were close to that of the stoichiometry

$$(PO_3)_x^{x-} + x\,SO_4^{2-} \rightarrow x\,PO_4^{3-} + x\,SO_3 \qquad (24)$$

(Calculated for loss of x S + $3x$ O per $Na_x(PO_3)_x$ = 78.5%).

The reactions of tetrametaphosphate, trimetaphosphate, and both soluble and insoluble metaphosphate showed similar trends with the initial formation of polymeric species of various lengths in each case, followed by the formation of tripolyphosphate and evolution of sulphur trioxide. The suggested sulphatophosphate species (Fig. 1, species VII) explain these results and its depolymerisation, by rupturing the bonds marked by arrows, produces tripolyphosphate and sulphur trioxide. A five-fold coordination of phosphorus atoms, in the species, can be achieved through dative bonding by their empty *d*-orbitals. P—O—S linkages have previously been reported [24] in compounds of the formulae $Na_3PS_2O_{10}$ and $Na_4P_2S_2O_{10}$.

The reactivity of the condensed phosphates and orthophosphate in the molten sulphate eutectic, based on their initial reaction temperatures, may be arranged in the order TMP ~ TTMP ~ MP > TPP > PP > OP. This order is the same as that for their Lux—Flood acid strength, based on their relative lack of oxide ions, and similar to those found in molten nitrates [13,14] and molten nitrite [15]. The high reaction temperatures of the condensed phosphates in the molten sulphate eutectic are attributed to the weak basic nature of the sulphate melt and in comparison with the reaction temperatures of the same species in molten carbonate [16], nitrite [15], perchlorates [17], and nitrates [13,14], the basicity of these melts may be arranged in the order carbonate > nitrite > perchlorate > nitrate > sulphate.

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