

THERMOGRAVIMETRIC-DIFFERENTIAL THERMAL ANALYSIS AND PAPER CHROMATOGRAPHIC STUDIES OF COMPLEX ALKALI-POLYMETAPHOSPHATES

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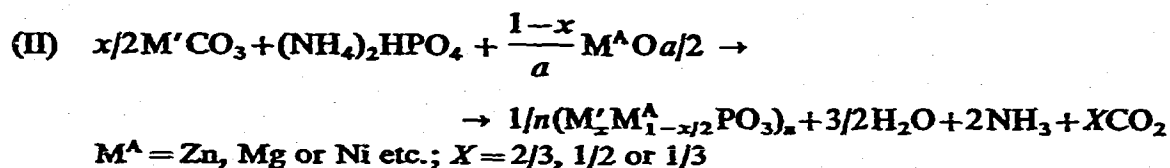
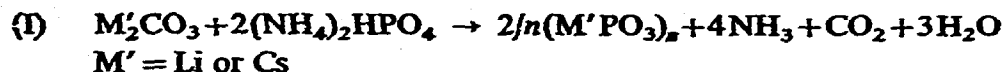
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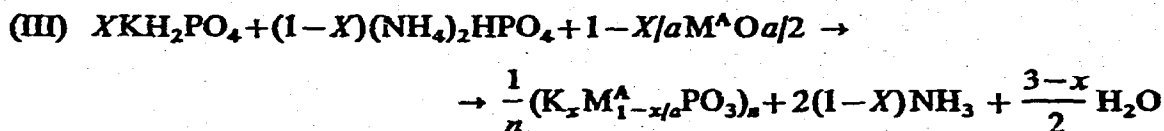
ABSTRACT

The polymerisation reactions leading to the formation of polyphosphates of the composition $(M'_x M''_{1-x/2} PO_3)_n$ where $M' = K$, or Cs and $M'' = Zn, Mg$ or Ni have been studied by thermogravimetric methods. Differential thermal analysis has been employed for the above reaction mixtures in case of potassium derivatives. TG and DTA curves confirm the formation of complex alkali polymetaphosphates of the composition as mentioned. The absence of lower phosphates and of other cyclic phosphates has been further confirmed by paper chromatographic studies of the above-mentioned complex derivatives as well as of many other alkali polymetaphosphates prepared in an analogous manner.

INTRODUCTION

Thermogravimetric and differential thermal analysis techniques have been used by many workers to study the thermal dehydration of orthophosphates. Thilo and Grauze¹ have studied the thermal dehydration of the orthophosphates of many cations and reported that the stable end products are tetrametaphosphates in some cases and crystalline polyphosphates in a few other cases. Boulle and Domraine-Berges² have reported the dehydration of potassium dihydrogen phosphate using the thermogravimetric analysis and the final end product reported was $(KPO_3)_n$. Osterheld and coworkers^{3,4} have studied in detail the condensation reactions of alkali metal hydrogen orthophosphates. Recently, Calvet et al.^{5,6} have studied quantitatively the thermal analysis of sodium and potassium dihydrogen phosphates. The simple and complex alkali polymetaphosphates have been prepared in these laboratories by the reactions represented below at 800°C.





where $M' = Li$ or Cs ; a is valency of M^A .

The molecular weights (M_n and M_w) of the complex derivatives are found to be lower than those of simple alkali polymetaphosphates. Audrieth and Hill⁷ have reported the formation of trimetaphosphates due to the depolymerization of polyphosphate melts in the presence of metal oxides. In view of the formation of ring phosphates in general in mixed metal phosphate systems the presence of trimetaphosphates as stable phases in these derivatives could also be anticipated. It was therefore, considered worth while to throw light on the composition of complex polymetaphosphate derivatives by thermal analysis. Mehrotra and Gupta⁸ have used thermogravimetry for establishing the composition of the complex sodium polymetaphosphates from the weight loss data. In the present study the composition of the derivatives mentioned above and their formation temperatures have been established from TG data. Differential thermal analysis has been used to follow the progress of the reaction and find out the formation of distinct phases at various temperatures.

Paper chromatographic methods have been widely used for quantitative separation, detection and differentiation of various phosphates⁹⁻¹¹. Griffith and Buxton^{12,13} and Thilo and Schuelke^{14,15} have been able to separate ring and chain phosphates by this technique. It has been shown that the thermal degradation of condensed phosphates and their hydrolytic and condensation reactions can be studied by this method. Morey¹⁶ reported the existence of a derivative of composition $[Na_4Ca(PO_3)_6]$ in the $Na_2O-CaO-P_2O_5$ system and considered it to be hexametaphosphate but Ohashi and Van Wazer¹⁷ showed it to be a trimetaphosphate derivative by chromatography. As the formation of some lower chain or ring phosphates might be expected during thermal dehydration of alkali hydrogen phosphates in presence of metal oxides, it was considered worth while to undertake a chromatographic investigation of the dehydration products.

EXPERIMENTAL

A Stanton "Mass Flow type" automatic direct recording thermobalance was used to follow the progress of the reactions.

The reaction mixtures were taken in a platinum crucible and heated gradually ($4^\circ C \text{ min}^{-1}$). The weight loss with the increase in temperature was recorded automatically; at a scanning speed of 6 in. h^{-1} . The differential thermal analysis of the reaction mixture consisting of $2/3KH_2PO_4$, $1/3(NH_4)_2HPO_4$ and $1/6$ (MgO or ZnO or $NiCO_3$) has been carried out with the help of a DTA apparatus¹⁸. The heating rate was kept at $6^\circ C \text{ min}^{-1}$ and ΔT vs. T was recorded with the help of Kipp and Zonen (BD-1) recorder at a Span of 2.5 mV.

For chromatographic studies, a chromatographic tank, micropipettes of 25 and 50 μl for applying the sample solution on the paper and an all glass spray were used.

Two types of eluents were used for the detection of these polyphosphates.

(1) *Ebel's acidic solvent*. This consists of a mixture of tertiary butyl alcohol (80 ml), water (20 ml) and formic acid (5 ml).

(2) *Pfrenge's acidic solvent*. This is a mixture of methanol (60 ml) trichloroacetic acid solution (10.3 ml) prepared by dissolving 100 g trichloroacetic acid in 500 ml water to which 22.7 ml of ammonia were added; acetic acid solution (5 ml) prepared by dissolving 20 ml acid in 80 ml water and water (12.5 ml).

Preparation of the sample solution

All the samples were prepared by fusion technique as reported earlier. Sodium trimetaphosphate and tetrametaphosphate were prepared by standard techniques. Approximately equimolar solutions of all these derivatives were prepared by dissolving a suitable amount of the compounds in water.

Whatman No. 1 chromatographic paper was taken for this purpose. 25 μl of reference as well as the sample solutions were then spotted on it at a distance of about 2.5 cm each. Care was taken to keep the spot size as small as possible. The paper was then hung in the chromatographic tank and ascending technique was used. The solvent was allowed to move for a definite period. The paper was taken out dried in air and sprayed with molybdate reagent. It was then dried, first in a current of hot air and then in an oven at 60°C for a few minutes. It was then placed under an ultraviolet source. Yellow spots of phosphomolybdate were developed which were marked with a pencil. R_f and R_g values were then measured.

RESULTS AND DISCUSSION

The thermogravimetric curves (Fig. 1) for the different reactions were obtained. From these curves it is evident that there is a rapid loss in weight up to 250–350°C but at higher temperatures the weight loss rate is slowed down. But the curves obtained in all these cases are continuous showing the absence of any intermediate stage in the reaction. In case of cesium and lithium polymetaphosphates, the weight becomes constant at lower temperature ($\sim 500^\circ\text{C}$) but in case of complex derivatives (Fig. 1) the constant weight is observed at higher temperatures. The complex potassium polymetaphosphate derivatives attain the constant weight below 600°C (Fig. 1). In all three proportions for lithium the temperature is $\sim 700^\circ\text{C}$ and for cesium derivatives it is $\sim 650^\circ\text{C}$. Thus, it is evident that any derivative formed above this temperature ($\sim 700^\circ\text{C}$) should correspond to the composition mentioned above. There is an interesting variation in the temperature of constant weight. It decreases with the increasing ratio of bivalent metal oxide or carbonate. Thus the weight loss data confirm the formation of the complex derivatives.

The DTA curves (Fig. 2) show that the first endothermic peak occurs at 130°C for the zinc and at 125°C for the magnesium and nickel system. This peak corresponds

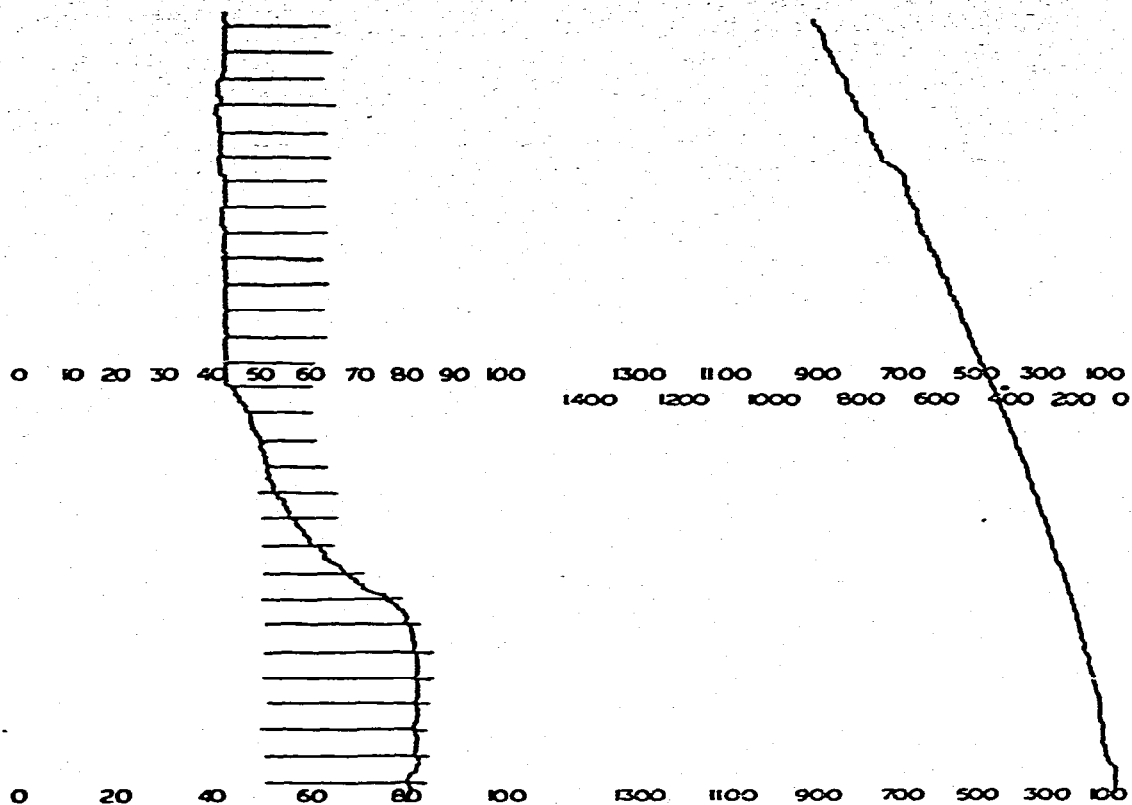


Fig. 1. TG curve for the reaction mixture $1/2\text{KH}_2\text{PO}_4$, $1/2(\text{NH}_4)_2\text{HPO}_4$ and $1/4\text{MgO}$.

TABLE 1

TEMPERATURE AT CONSTANT WEIGHT AND WEIGHT LOSS OF REACTION MIXTURE FOR THE COMPLEX POTASSIUM POLYMETAPHOSPHATE OF ZINC, MAGNESIUM AND NICKEL

| Composition of the derivative | Weight (mg) of reaction mixture | Weight in (mg) of the product | Loss in weight in (mg) | | Temp. at constant weight |
|--|---------------------------------|-------------------------------|------------------------|-------|--------------------------|
| | | | Calc. | Found | |
| $(\text{K}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$ | 150 | 120 | 33 | 30 | 580 |
| $(\text{K}_{1/2}\text{Zn}_{1/4}\text{PO}_3)_n$ | 120 | 95 | 25 | 25 | 460 |
| $(\text{K}_{1/3}\text{Zn}_{1/3}\text{PO}_3)_n$ | 150 | 106.7 | 42 | 43.3 | 420 |
| $(\text{K}_{2/3}\text{Mg}_{1/6}\text{PO}_3)_n$ | 150 | 115 | 34 | 35 | 580 |
| $(\text{K}_{1/2}\text{Mg}_{1/4}\text{PO}_3)_n$ | 150 | 109 | 40 | 41 | 460 |
| $(\text{K}_{1/3}\text{Mg}_{1/3}\text{PO}_3)_n$ | 150 | 102 | 48 | 48 | 440 |
| $(\text{K}_{2/3}\text{Ni}_{1/6}\text{PO}_3)_n$ | 150 | 115 | 35 | 35 | 520 |
| $(\text{K}_{1/2}\text{Ni}_{1/4}\text{PO}_3)_n$ | 151.6 | 114.7 | 36.9 | 35 | 460 |

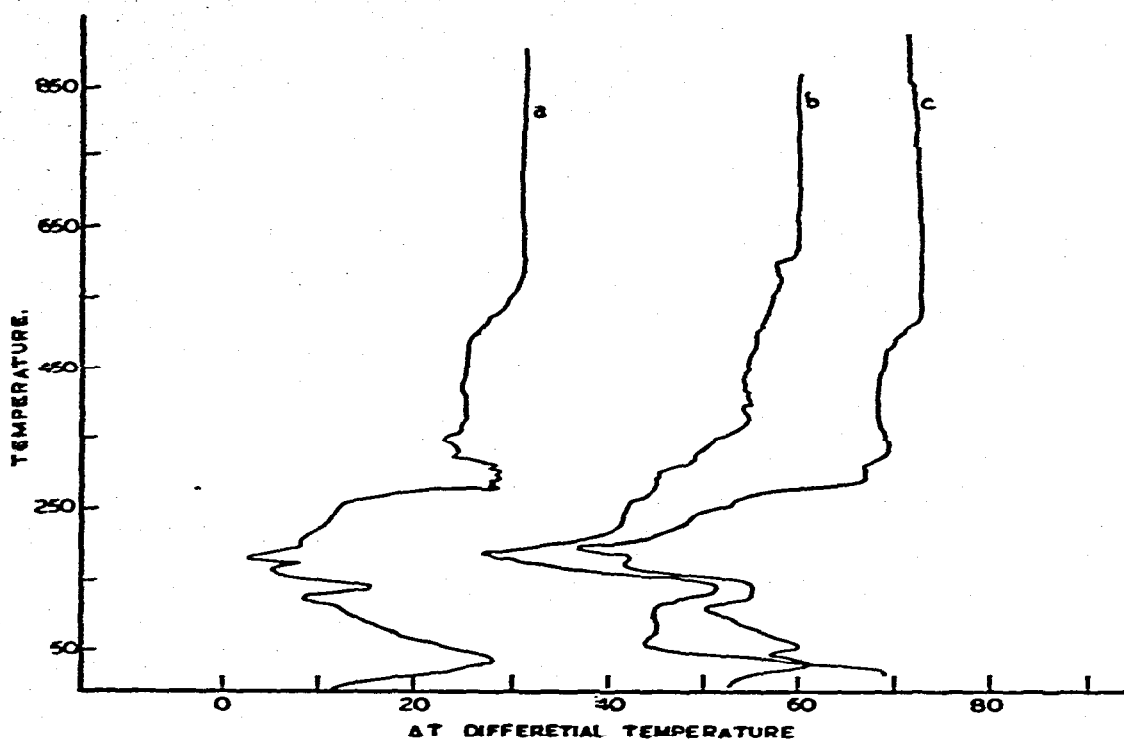


Fig. 2. DTA curves for the reaction mixture $2/3\text{KH}_2\text{PO}_4$, $1/3(\text{NH}_4)_2\text{HPO}_4$ and (a) $1/6\text{ZnO}$; (b) $1/6\text{MgO}$; (c) $1/6\text{NiCO}_3$.

TABLE 2

THERMOGRAVIMETRIC ANALYSIS OF THE REACTION MIXTURE USED FOR THE FORMATION OF THE COMPLEX DERIVATIVES OF Li AND Cs

| Composition | Amount of mixture taken | Weight loss | | Temp. at constant weight |
|---|-------------------------|-------------|--------|--------------------------|
| | | Calc. | Found | |
| $[\text{LiPO}_3]_n$ | 0.3380 | 0.1662 | 0.1640 | 500 |
| $[\text{Li}_{2/3}\text{Zn}_{1/6}\text{PO}_3]_n$ | 0.4767 | 0.1938 | 0.1925 | 700 |
| $[\text{Li}_{1/2}\text{Zn}_{1/4}\text{PO}_3]_n$ | 0.6835 | 0.2885 | 0.2887 | 675 |
| $[\text{Li}_{1/3}\text{Zn}_{1/3}\text{PO}_3]_n$ | 0.5145 | 0.2053 | 0.2100 | 650 |
| $[\text{CsPO}_3]_n$ | 0.6579 | 0.2200 | 0.2250 | 500 |
| $[\text{Cs}_{2/3}\text{Zn}_{1/6}\text{PO}_3]_n$ | 0.3824 | 0.1210 | 0.1150 | 650 |
| $[\text{Cs}_{1/2}\text{Zn}_{1/4}\text{PO}_3]_n$ | 0.4857 | 0.1700 | 0.1630 | 625 |
| $[\text{Cs}_{1/3}\text{Zn}_{1/3}\text{PO}_3]_n$ | 0.3293 | 0.1160 | 0.1120 | 600 |

to the evolution of NH_3 and water from the reaction mixtures. Another strong endothermic peak has been observed around 190–200°C for all three systems. This peak corresponds with the dehydration process during which water is lost. The dehydration of KH_2PO_4 starts at 208°C and is completed at 258°C with the formation of $(\text{KPO}_3)_n$ ³. This is not true for mixed alkali polymetaphosphates. Conversion into polyphosphates is not completed at such low temperatures and the endothermal process is over only around 580°C. A similar situation is observed in the TG curve. There the curve also shows a constant weight at this temperature. In case of mixed metal systems the "tailing off" of the endothermal peak in the differential thermograms could be attributed to the decomposition of intermediate phases formed during the heating process. These intermediate phases could be complex pyrotrimeta- or tripolyphosphates. The presence of polyvalent cations seems to offer possibilities of the formation of trimetaphosphates in the complex polymetaphosphate systems under study. Thus it can be concluded that the derivatives prepared at 800°C correspond to the composition $[\text{M}'_x\text{M}''_{1-x/2}\text{PO}_3]_n$ and any other lower cyclic or chain phosphates are decomposed² below 600°C.

The R_F and R_g values of lithium and cesium polymetaphosphates and their complex derivatives along with sodium polymetaphosphate and other reference compounds are given in Table 3.

From these values it can be seen that lithium and cesium polymetaphosphate and their complex derivatives have values which are very close to that for Graham's salt and do not correspond to any other reference compound (lower phosphate) indicating the long chain polymeric nature of complex derivatives similar to that of Graham's salt. A very weak spot due to trimetaphosphates is observed which is probably due to the hydrolysis of the polymetaphosphates. A trailing effect¹⁹ was observed in a few cases but the R_F and R_g values could be calculated without much difficulty.

TABLE 3

R_F AND R_g VALUES OF COMPLEX ALKALI POLYMETAPHOSPHATE IN EBEL'S ACIDIC SOLVENT

| Compound | Run 1 | 20 h | Run 2 | 22 h |
|---|-------|-------|-------|-------|
| | R_F | R_g | R_F | R_g |
| NaH_2PO_4 (R) | 0.611 | — | 0.623 | — |
| $\text{Na}_2\text{P}_2\text{O}_7$ (R) | 0.467 | 0.764 | 0.473 | 0.771 |
| $\text{Na}_3\text{P}_3\text{O}_9$ (R) | 0.411 | 0.673 | 0.420 | 0.680 |
| $\text{Na}_2\text{H}_2\text{P}_2\text{O}_{12}$ (R) | 0.311 | 0.509 | 0.320 | 0.512 |
| $(\text{NaPO}_3)_n$ (R) | 0.033 | 0.054 | 0.034 | 0.055 |
| $(\text{LiPO}_3)_n$ (S) | 0.028 | 0.045 | 0.030 | 0.046 |
| $(\text{Li}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$ (S) | 0.056 | 0.090 | 0.057 | 0.091 |
| $(\text{Li}_{1/2}\text{Zn}_{1/4}\text{PO}_3)_n$ (S) | 0.066 | 0.110 | 0.066 | 0.110 |
| $(\text{Li}_{1/3}\text{Zn}_{1/3}\text{PO}_3)_n$ (S) | 0.082 | 0.130 | 0.082 | 0.130 |
| $(\text{CsPO}_3)_n$ (S) | 0.027 | 0.039 | 0.030 | 0.042 |
| $(\text{Cs}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$ (S) | 0.039 | 0.055 | 0.040 | 0.056 |
| $(\text{Cs}_{1/2}\text{Zn}_{1/4}\text{PO}_3)_n$ (S) | 0.060 | 0.078 | 0.065 | 0.079 |

TABLE 4

R_F AND R_g VALUES OF COMPLEX ALKALI POLYMETAPHOSPHATES IN PFRENGLE'S (METHANOL) ACIDIC SOLVENTS

| Compound | Run 1 R_F | 15 h R_g | Run 2 R_F | 17 h R_g |
|---|----------------|---------------|----------------|---------------|
| NaH_2PO_4 (R) | 0.840 | — | 0.860 | — |
| $\text{Na}_4\text{P}_2\text{O}_7$ (R) | 0.800 | 0.950 | 0.820 | 0.950 |
| $\text{Na}_3\text{P}_3\text{O}_9$ (R) | 0.680 | 0.810 | 0.700 | 0.810 |
| $\text{Na}_2\text{H}_2\text{P}_4\text{O}_{12}$ (R) | 0.640 | 0.750 | 0.660 | 0.760 |
| $(\text{NaPO}_3)_n$ (R) | 0.026 | 0.031 | 0.027 | 0.032 |
| $(\text{LiPO}_3)_n$ (S) | 0.024 | 0.030 | 0.025 | 0.030 |
| $(\text{Li}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$ (S) | 0.043 | 0.048 | 0.044 | 0.048 |
| $(\text{Li}_{1/2}\text{Zn}_{1/4}\text{PO}_3)_n$ (S) | 0.042 | 0.047 | 0.045 | 0.051 |
| $(\text{Li}_{1/3}\text{Zn}_{1/3}\text{PO}_3)_n$ (S) | 0.039 | 0.045 | 0.041 | 0.047 |
| $(\text{CsPO}_3)_n$ | 0.020 | 0.023 | 0.020 | 0.023 |
| $(\text{Cs}_{2/3}\text{Zn}_{1/6}\text{PO}_3)_n$ | 0.022 | 0.025 | 0.023 | 0.026 |
| $(\text{Cs}_{1/2}\text{Zn}_{1/4}\text{PO}_3)_n$ | 0.040 | 0.044 | 0.043 | 0.048 |

Thus it is clear that in all the cases of complex lithium and cesium polymetaphosphate derivatives the R_F and R_g values correspond to those for Graham's salt and the chromatogram shows the absence of any other component. Hence, the long chain polymeric nature of these complex derivatives is further elucidated.

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