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HIGH TEMPERATURE THERMAL PROPERTIES OF KH_2PO_4: PHASE TRANSITIONS AND DECOMPOSITIONS

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ABSTRACT

Phase transitions and the thermal decomposition of KH_2PO_4 have been examined from room temperature to above 300 °C by means of hot-stage microscopy, isothermal gravimetry and differential scanning calorimetry. Phase transitions at 198 and 242 °C are confirmed, with corresponding enthalpy changes 4.2 and 2.3 kJ mole^{-1}, but no evidence has been found of a transition reported near 110 °C. The thermodynamic and other evidence suggest a structural change at 198 °C while the change at 242 °C is less profound, perhaps involving only changes in the form of the hydrogen bonding. Thermal decomposition occurs in four stages, under conditions of free vapour escape, with the loss of one-quarter of a mole of water per formula unit of KH_2PO_4 in each stage. The products of each stage of decomposition are tentatively identified.

INTRODUCTION

Potassium dihydrogen phosphate, KH_2PO_4, is the representative member of the KH_2PO_4 family of isomorphous, hydrogen-bonded ferroelectric materials and, as such, its physical properties engender much interest[1]. The proton-ordered, ferroelectric phase (phase III in Rapoport's nomenclature)[2] of KH_2PO_4 is well known to convert to the proton-disordered, paraelectric phase, II, at -152 °C.

Recently, further high temperature phase transitions have been observed in KH_2PO_4; at 110–115 °C by Poplavko and colleagues, using dielectric[3] and thermoelastic[4] methods; at 180 ± 3 °C by O'Keeffe and Perrino[5] using conductivity measurements, and by Grünberg et al.[6], using dielectric and IR methods (phase II → II′, following Rapoport); and at 233 °C in a sealed container by Rapoport[2], using high pressure DTA (phase II′ → I). Phase II is the stable phase at room temperature, while phase II′ is metastable on account of its slow rate of reversion at room temperature to II. Finally, KH_2PO_4 melts[2, 5] (phase I → liquid) at 259–260 °C, in a sealed container.

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TABLE 1

HIGH TEMPERATURE THERMAL BEHAVIOUR OF KH_2PO_4

Heating rate	*Atmosphere*	*Method*	*Phase transitions*				*Decomposition*	*Remarks*	*Ref.*
			Near 100°C	*II → II′*	*II′ → I*	*I → liquid*			
Quasi-static	Equilib. press. of H_2O vap.	Conductivity		180°C (becomes opaque)		260 ± 1°C (sealed)			5
Quasi-static	Air	Dielectric (10 MHz) and IR		180 ± 3°C (slow; shatters)					6
Quasi-static	Air	Dielectric (10 MHz)		175°C (slow; slowly reversible)			Surface decomp. when exposed	< 0.15% mass loss in 30 min above transition	8
		IR reflection		160–190°C					
~1°C min^{-1}	Air	Dielectric (microwave)	115°C (reversible)				210°C (prob. decomp.)[a]		3
		TGA	None				200°C		
Quasi-static	Air	Linear expansion	110°C (reversible)				204°C (prob. decomp.)[a]		4
Quasi-static	Air	NMR line-width	105°C (release of trapped H_2O)	174°C (observed by decomp.)					18
Quasi-static	Flushed with dry N_2	Conductivity (upper limit: 180°)	110–112°C						13(a)

Quasi-static	Flushed with dry N_2	Conductivity	100°C	180°C (becomes opaque)	Suggest decomp. above 180 °C, as well	Vacuum evaporated electrodes	13(b)
Quasi-static	Vacuum and sealed	Positron annihilation		174 ± 6 °C (slowly reversible)		Essentially same results, vacuum or sealed	12
Quasi-static	Air (?)	X-ray diffraction (powder and single crystal)	? — no change in symmetry (tetragonal)	187°C (shatters, becomes monoclinic)			11
Quasi-static	Air (?)	Raman scattering		~177°C (onset: 150°C)			10
~0.01 °C min^{-1}		Light scattering		~175°C (irreversible) in expt. time)		< 0.01 % mass loss over expt. time	9
Quasi-static	Air (?)	NMR line-width		Centred at 175°C			7
	Air (?)	Spin-lattice relax. time		174°C (slowly reversible)			
	Air	X-ray diffraction				Breakdown of lattice towards 200 °C	
	Air	Neutron scattering				Broadening of scattered peak disappears above 175°C	

TABLE 1 *(continued)*

Heating rate	*Atmosphere*	*Method*	*Phase transitions*				*Decomposition*	*Remarks*	*Ref.*
			Near 100°C	*II → II′*	*II′ → I*	*I → liquid*			
	Air	IR absorption		~180°C (slowly reversible)	Further changes above 185°C, not due to decomp.			Absorption in 400 cm^{-1} region disappears	7
5°C min^{-1}		DTA		171°C (onset)			Noticeable from 213°C		
5°C min^{-1}		TGA					Noticeable 200°C complete 340°C (− H_2O)		
60°C min^{-1}	Sealed capsules	DTA, high pressures		190–197°C (depends on heating rate, irreversible in expt. time)	233°C (much hysteresis)	259 ± 1°C (repeatable)			2

[a] Interpretation by authors of the present paper.

Grünberg et al.[6] have predicted the highest temperature phase-transformation on theoretical grounds, related to the existence of the low-temperature ferroelectric phase, and by comparison with the phase behaviour of KD_2PO_4 and of RbH_2PO_4.

Although a number of phase studies[2, 6–12] have tended to confirm the transformation near 180°C (cf. Table 1), there is some possibility of confusion with the thermal decomposition[14, 15] of KH_2PO_4, which commences at about 200°C; Kiehl and Wallace[16] report measurable water vapour pressures above KH_2PO_4 from 170°C. As a result, the reality of the physical observations has been questioned, with the suggestion[17, 18] that these are associated with decomposition instead. No confirmation of the 233°C transition (II′ → I) has been published, although Blinc et al.[7] did note further changes in the IR spectrum, not due to decomposition, above 185°C.

The thermal decomposition itself is, indeed, complicated[14–16, 19, 20]. A variety of condensed phosphates are formed, with loss of water, at temperatures dependent upon the physical state of the sample, the nature of the surrounding atmosphere, and the temperature programme applied. The final decomposition product is potassium (poly)metaphosphate, $(KPO_3)_x$, known as Kurrol's salt.

The present study confirms the distinction between the phase transitions and the thermal decomposition. The combined use of the complementary techniques of hot-stage microscopy (HSM), differential scanning calorimetry (DSC), and isothermal gravimetry (ITG), provides a comprehensive picture of the thermal behaviour of KH_2PO_4. Thermodynamic data on the phase transitions are reported, and features of the thermal decomposition are clarified.

EXPERIMENTAL

Materials and apparatus

The KH_2PO_4 used was of analytical grade (Hopkins and Williams). Single crystals with diameters in the range 1–3 mm, and ground material with crystallite diameters in the range 1–50 μm were used. The major instrumentation was as follows: a Perkin-Elmer DSC-2 differential scanning calorimeter; a Cahn RG electrobalance and microfurnace; and a Leitz Ortholux polarising microscope with hot stage. DSC and HSM observations were made on samples which were open to the atmosphere, or which were sealed (in glass capillary tubes for HSM, and in standard cold-welded aluminium sample pans for DSC). It may be noted, as a warning to others, that the phosphoric acid fumes evolved eventually caused major corrosion damage to the DSC sample holders. Heating rates in the range 0–360°C min^{-1} were used in various experiments, but a rate of $\sim$20°C min^{-1} was chosen for comparison of DSC and HSM observations. ITG measurements were made on samples rapidly heated in vacuum to the chosen temperatures and then maintained at those temperatures until no further mass loss was recorded. The extent of the observed decomposition stages was the same for the powder and the single crystals. The powder samples, however, decomposed more rapidly at a given temperature. The temperatures in each apparatus were calibrated by reference to the temperatures of known transitions in standard materials. The DSC temperatures are accurate to ±1 °C.

Enthalpy determinations

The enthalpies of the two high-temperature crystalline phase transitions were determined from the DSC records for single crystals contained in sealed pans. The areas of the corresponding endotherms were determined by planimetry and converted to enthalpy values through calibration data for the fusion of pure metals (In, Sn, Pb and Zn). The onset of thermal decomposition prevented the determination of the enthalpy of melting of KH_2PO_4.

Because of the extensive overlapping of the transitions in the powder, only the total enthalpy of the combined transitions is reported. The behaviour of some samples was studied while they were immersed in a thermally stable oil[21], to reduce thermal decomposition of powder samples.

RESULTS

Hot-stage microscopy (HSM)

When single crystals of KH_2PO_4 are heated (20 °C min^{-1}), under the polarising microscope, the first observed change is a crystalline phase transition at 192–207 °C (corresponding to II → II′). The transition is initiated at scattered centres in the individual crystallites, passing through each in intersecting waves observable as changes in birefringence. The crystal then shatters, becoming opaque. At slightly higher temperatures, 210–230 °C, the onset of thermal decomposition can be observed, since a liquid phase, believed to be a product of thermal decomposition, forms on the fracture surfaces within the crystal. As the fractures slowly fill with liquid, the crystal becomes transparent again. A few bubbles can be observed moving through the liquid. At 240–250 °C waves of birefringence changes again pass through the remaining solid regions of the crystal. This is the temperature range observed on the DSC for the second phase transition (II′ → I). As the reported "melting point" in an open container[22], 253 °C, is approached, surface melting is observed. Complete "melting" is accompanied by frothing and followed by formation of a skin on the liquid surface. The liquid activity subsides (290 °C) while the amount of skin material increases. At 300 °C a final burst of vapour release occurs and only hollow skin structures remain. Melting of the skin product, potassium (poly)metaphosphate[23], occurs at 810 °C, as observed using a thermocouple hot-stage microscope[24].

For KH_2PO_4 powder samples, with their much larger surface areas, onset of thermal decomposition is observed at lower temperatures (200–210 °C). The crystallites rapidly become coated with viscous liquid and coalesce. The two crystalline phase transitions are observed as sudden birefringence changes in individual KH_2PO_4 crystallites throughout the temperature range 200–240 °C. At 240 °C liquefaction is complete, and subsequent frothing and skin formation occurs as described for single crystals.

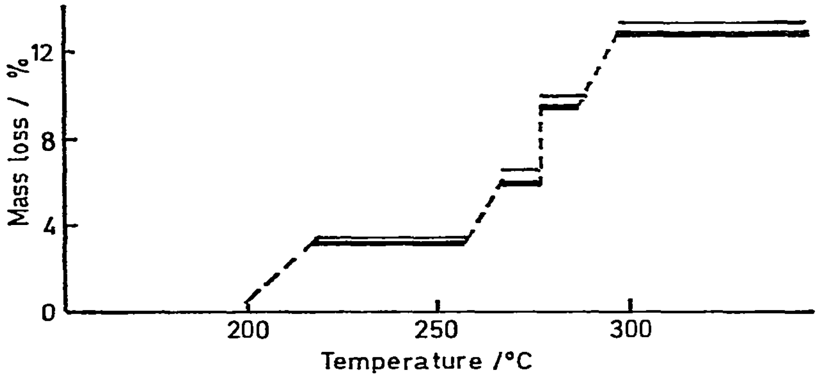

Fig. 1. A composite plot of total mass loss vs. temperature, constructed from separate isothermal gravimetric records. Thick lines represent observed mass losses; thin lines represent the mass loss expected for a loss of one-quarter of a mole of water, per formula unit of KH_2PO_4, per step.

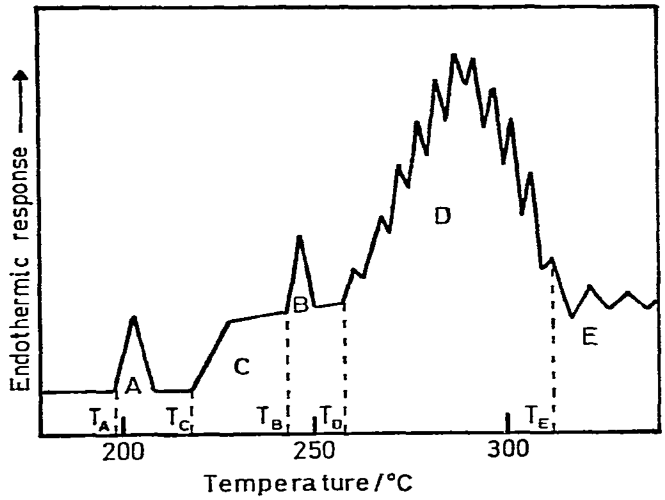

Fig. 2. Composite schematic DSC record for single crystals of KH_2PO_4, constructed from many repetitions on separate samples in sealed containers.

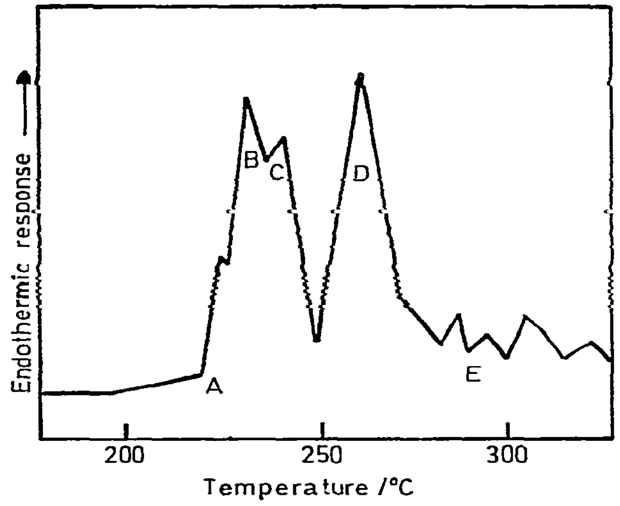

Fig. 3. Composite schematic DSC record for KH_2PO_4 powder, constructed from many repetitions on separate samples in sealed containers.

Decomposition was suppressed in samples sealed in glass capillaries and did not occur to a marked extent below the observed melting point of ~300 °C, at a heating rate of 20 °C min^{-1}.

Isothermal gravimetry (ITG)

The overall stoichiometry of the thermal decomposition of KH_2PO_4 corresponds to

$$KH_2PO_4 \rightarrow KPO_3 + H_2O$$

where KPO_3 represents the complex (poly)metaphosphate, $(KPO_3)_x$.

The details of the processes involved are complicated[14–16], but Gallagher[25] has recently noted a sequence of four peaks in the derivative thermogram, with decomposition commencing at about 219 °C, at a heating rate of 5 °C min^{-1}. In the present investigation four ITG plateaus were observed in vacuum for KH_2PO_4 samples, powder or single crystals, each rapidly heated in steps to temperatures in the range 200–430 °C. The cumulative mass losses at the plateaux closely follow the sequence 3.3, 6.6, 9.9 and 13.2% (Fig. 1), corresponding to the loss of one-quarter of a water molecule per KH_2PO_4 formula unit between each plateau.

Differential scanning calorimetry (DSC)

The detailed form of the DSC records is dependent upon sample and operating conditions. For the purposes of discussion, schematic DSC records for KH_2PO_4 samples, single crystal (Fig. 2) and powder (Fig. 3), are presented. The assignment of peaks for powder samples (Fig. 3) is somewhat tenuous, having been done largely by reference to the results for single crystals (Fig. 2). The endotherms A, B, C, D and E with their corresponding onset temperatures T_A, T_B, T_C, T_D and T_E are associated with the following thermal events.

A, *B* and T_A, T_B. Endotherms A and B correspond to the two high-temperature crystalline phase transitions[2] of KH_2PO_4. The existence of the higher temperature transition, B (II′ → I)[2] is thus confirmed. The metastable nature of the intermediate phase II′, formed between T_A and T_B, with respect to the room temperature phase II at temperatures below T_A is also confirmed. A single crystal heated to above 250 °C undergoes both transitions and passes into the high-temperature phase, I, above T_B. Upon immediate cooling to room temperature the crystal reverts rapidly to phase II′, and then slowly back to the room temperature phase II, over a period of several days, as confirmed by reheating different samples after the lapse of increasingly longer periods. The value of T_B on cooling is ~80° lower than on heating. T_A, on heating, varies greatly from crystal to crystal.

DSC records approaching those of powder samples (see below) were observed when successively greater numbers of smaller crystals with the same total mass were heated through the transitions. For powder samples, transition A is dispersed over the temperature range 200–250 °C, overlapping extensively with B. Reversal of the transitions is somewhat obscured by concurrent thermal decomposition during heating cycles when unsealed containers are used.

C, D, E and T_C, T_D, T_E. Endotherm C results from the thermal decomposition of KH_2PO_4 in the solid state, for it corresponds in temperature range, and in mass loss on interruption, with the loss of one-quarter of a water molecule per KH_2PO_4 formula unit. The onset temperature, T_C, varies greatly with heating rate. In single crystal samples T_C may be below T_A or above T_B. For powder samples, T_C coincides approximately with T_A and T_B, but the shape of C is again greatly affected by heating rate. At higher heating rates C is skewed upscale, eventually merging with D. At lower heating rates C moves downscale, merging with, and obscuring, A and B. Endotherm D results from melting together with decomposition in the liquid state. It corresponds to a cumulative mass-loss of 10%, or to three-quarters of a mole of water per KH_2PO_4 formula unit. T_D was determined as the junction between the smaller, smoother endotherm C and the steeply rising, irregular endotherm D in single crystal samples. The value of T_D corresponds well to the melting point of KH_2PO_4 as reported by Rapoport[2] and O'Keeffe and Perrino[5], i.e. 259–260 °C. For powder samples, D was skewed slightly upscale at higher heating rates. Endothermic region E results from the last high-temperature decomposition processes. E has a highly irregular trace but an endotherm can often be distinguished at the low temperature end of E, 300 °C, which corresponds to the burst of vapour release seen by HSM at that temperature, and also corresponds in temperature to the final mass-loss, as observed by ITG, of 13%.

TABLE 2

TRANSITION ENTHALPIES AND ENTROPIES

Phase transition	Onset temp. (°C)	ΔH (kJ mole^{-1})	ΔS (J K^{-1} mole^{-1})	Ref.
III → II	−152	~0.4	3.2, 2.0	1
II → II′ (A, single crystal in air)	198 ± 3 (53)	4.2 ± 0.3 (8)	8.9	Present work
II → II′	171	4.6 ± 0.6[a]	10.4	7
II → I (B, single crystal in air)	242 ± 3 (17)	2.3 ± 0.4 (8)	4.4	Present work
A + B (single crystal in air)		6.5		Present work
A + B (powder in air)		6.8 ± 0.6 (8)		Present work
A + B (powder in oil)		6.2 ± 0.6 (7)		Present work

Note: Standard deviations are given; the figures in brackets represent the number of observations of the quantities concerned.

[a] Value dependent on sample crystallinity; grinding reduces ΔH.

Thermodynamic data

Table 2 gives the temperatures, enthalpies and entropies determined for the two high-temperature crystalline phase transitions.

DISCUSSION

Phase transitions in KH_2PO_4

A phase transition at −152°C in KH_2PO_4 is well established[1]. It occurs between a proton-ordered ferroelectric phase and a proton-disordered paraelectric phase, with an entropy increase of about 3 JK^{-1} $mole^{-1}$. The transition at about 110°C (Table 1) has not been observed in the present study, either by HSM or by DSC, and we support the suggestion[18] that the effects reported are due to the (partial) release of trapped water, although the transition has elsewhere[3, 4] been rather tentatively designated "reversible". X-Ray lattice expansion studies[26] show no discontinuity between 26 and 151 °C.

The phase transition near 180°C, II → II′, is by now established with certainty; it is rather sluggish, and increasing the heating rate from quasi-static values to above 5 °C min^{-1} raises the transition temperature to nearly 200 °C.

The room-temperature stable phase, II, crystallizes in the tetragonal space group[26, 27] $I\bar{4}2d$, while phase II′ is monoclinic[7, 8, 11, 18], with space group $P2_1$ or $P2_1/m$. The assignment of space groups is supported by the observation of similar crystal lattice changes in phase transitions[8, 18, 28] in KD_2PO_4 and in RbH_2PO_4.

The reverse transition, II′ → II, is very slow, and only occurs to a small extent on extended storage of the crystals at room temperature. The entropy change is about 9 JK^{-1} $mole^{-1}$ (Table 2); the transition is thus much more disruptive than the low-temperature proton-disorder transition (III → II), whose entropy change is roughly one-third of the II → II′ entropy change.

The phase transition at about 240 °C in a sealed container (II′→I) is confirmed[2, 8] by the present work. The entropy change is about 4.4 JK^{-1} $mole^{-1}$.

It is interesting to speculate briefly on the natures of these two high-temperature transitions.

In the paraelectric phase, II, the hydrogen atoms are strongly attached to the PO_4 groups, so that the most common group may be formulated[27] as $PO_2(OH)_2$, with some $PO_3(OH)$ and $PO(OH)_3$ groups as well. The hydrogen atoms participate in hydrogen bonds between adjacent phosphate tetrahedra.

The phase transition II → II′ (at T_1 in the nomenclature of Grünberg et al.[8]) is ascribed to some change connected with the PO_4 group, rather than with the hydrogen bonding, since "many crystals containing the PO_4 group undergo a transition in the vicinity of 175 °C, and neither deuteration of KH_2PO_4 nor substitution of K by Rb changes T_1". At the same time, She and Pan[10] note that a broad Raman spectral feature of B_1 symmetry, near 2500 cm^{-1}, disappears during the II → II′ transition. This spectral feature is ascribed to coupled motions of the hydrogen bond network. It thus seems that the onset of some hindered rotation of the PO_4 groups[7], which would indeed interfere with coupled hydrogen motions, is a possible cause of this transition. This conclusion tends to be supported by conductivity[5] and positron annihilation[12] studies, which associate the transition with the formation of hydrogen bond defects (D, or doubly proton occupied, and L, or empty, hydrogen bonds). NMR studies[17, 18, 28] have tended to discount the change as resulting from the onset of PO_4 rotation alone, but this objection seems to disappear[18] with the more recent confirmation of a tetragonal-to-monoclinic structural change involved in the II → II′ transition.

Grünberg et al.[8] have predicted the occurrence of the highest temperature phase change, II′ → I (at T_p in their nomenclature), by analogy with similar changes in KD_2PO_4 and RbH_2PO_4. This transition is ascribed to changes in the hydrogen bonding when, according to the model of Imry et al.[29], proton tunnelling between the two minima of the hydrogen bond almost ceases and the hydrogen becomes more permanently attached to one of the hydrogen-bonding oxygens. It is suggested that one proton is attached to an upper corner of the PO_4 tetrahedron, and the other proton to a lower corner (whereas in the ordered ferroelectric phase both protons are attached to lower corners of the tetrahedron[4] — the designation, "upper" and "lower", is arbitrary, but refers to orientations relative to the unique *c*-axis of the structure).

The entropy changes observed in the present study tend to support this distinction between the two transitions (insofar as purely numerical values can, without reference to physical happenings) in that the entropy change in the II → II′ transition is large (9 JK^{-1} $mole^{-1}$), appropriate to a structural change, whereas the entropy changes for the III → II and II′ → I transitions are much smaller, and close to each other in value (3 and 4.4 JK^{-1} $mole^{-1}$, respectively).

Thermal decomposition

The thermal decomposition of KH_2PO_4 is complex and has been the subject of much discussion[14], but the more recent work of Thilo and Grunze[20] and of Brun[15] appears to have solved some of the outstanding problems, and certainly clarifies much of the earlier work.

Distinction has to be drawn[20] between decomposition under conditions where product water is rapidly removed when the decomposition rate is controlled by chemical and topochemical considerations, and decomposition in the presence of significant water vapour pressures, when equilibria are readily attained. Under an equilibrium pressure of water vapour KH_2PO_4 appears to decompose directly[16] to potassium (poly)metaphosphate. On heating at slow rates (0.2°C min^{-1}) in air, under conditions which possibly restrict the escape of evolved water vapour, there is an arrest in mass loss between 230 and 280°C but formation of a definite intermediate compound has been denied[15, 20] because of variations in the mass loss corresponding to the arrest, of from 0.3 to 0.7 moles of water per formula unit of KH_2PO_4, depending on the experimental conditions. The arrest is ascribed[20] to the formation of an impermeable skin of the (poly)metaphosphate around the crystals, which prevents further decomposition until the internal water vapour pressure rises sufficiently to burst the skin. This description is rather strikingly illustrated by our HSM observations.

When KH_2PO_4 is heated directly to a fixed temperature in an open container, intermediate compounds may be formed; Thilo and Grunze[20] noted just one intermediate which formed between 200 and 250 °C, with formula $2KH_2PO_4 \cdot K_2H_2P_2O_7$ or, better, $K_4H_6(PO_4)_2P_2O_7$. However, under conditions of essentially free vapour flow in air (maximum mass of sample, 21 mg) or in vacuum (as in the present ITG work, with masses of < 10 mg) four discontinuities appear in the mass-loss curves as a function of temperature. Each of the four plateaux in our ITG experiments (Fig. 1) corresponds to the loss of one-quarter of a mole of water per formula unit of KH_2PO_4. Possible compositions of the decomposition intermediates are discussed in the following paragraphs.

The first step, commencing at about 200 °C according to the ITG observations (Gallagher[25] reports 219 °C), corresponds to

$$KH_2PO_4 \rightarrow \tfrac{1}{4}\,[K_4H_6(PO_4)_2P_2O_7] + \tfrac{1}{4}\,H_2O \qquad (1)$$

This intermediate, a "lattice complex", has been clearly identified by Boullé et al.[19], Thilo and Grunze[20], and Brun[15].

The second step, commencing at 260 °C under vacuum and with a product stable to about 280 °C, corresponds to

$$\tfrac{1}{4}\,[K_4H_6(PO_4)_2P_2O_7] \rightarrow \tfrac{1}{2}\,K_2H_2P_2O_7 + \tfrac{1}{4}\,H_2O \qquad (2)$$

Gallagher's differential thermogravimetric (DTG) curve, under free vapour flow, yields a rough value of 260 °C for the onset of this reaction while Boullé et al.[19] (at the slower heating rate of 2.5 °C min^{-1}, probably in air but with restricted vapour flow) observe accelerated mass loss from about 285 °C.

The intermediate, dipotassium dihydrogen pyrophosphate, is well-established [15, 19, 23]. Kiehl and Wallace[16], on the basis of vapour pressure studies, have claimed that $K_2H_2P_2O_7$ cannot be prepared by heating KH_2PO_4 because "its dissociation pressure at lower temperatures is higher than that of the orthophosphate (KH_2PO_4) when its forms metaphosphate under the same conditions". However, their equilibrium data[16] show that the dissociation pressure of the pyrophosphate is lower than that of the orthophosphate above 240 °C so that, if the temperature is rapidly raised (5–20 °C min^{-1}) above 240 °C, as in the present work and in that of Gallagher[25], the pyrophosphate is stable.

The third stage of the decomposition corresponds to

$$\tfrac{1}{2}\,K_2H_2P_2O_7 \rightarrow \tfrac{1}{4}\,[K_4H_2P_4O_{13}] + \tfrac{1}{4}\,H_2O \qquad (3)$$

The onset temperature found, 280 °C, compares well with that from Gallagher's DTG curve[25]. Hackspill and Lauffenberger[30] (conditions uncertain) report a lower onset temperature, 250 °C, while Boullé et al.[19] indicate onset at 315 °C (at a low heating rate, cf. second step above).

Neither Thilo and Grunze[20] nor Brun[15] report a similar intermediate product;

Brun has studied the thermal behaviour of $K_2H_2P_2O_7$ directly and reports that decomposition, at a heating rate of 0.2 °C min^{-1} and probably in air with restricted vapour flow, commences at about 200 °C and continues without discontinuities to 250 °C, with the formation of potassium (poly)metaphosphate. Apparently, at greater heating rates the latter direct decomposition is bypassed in favour of reaction (3).

Similar observations to those which we report on the decomposition of $K_2H_2P_2O_7$ to $K_4H_2P_4O_{13}$ (ref.30) and of KH_2PO_4 to $K_4H_2P_4O_{13}$ (ref. 31) have previously been reported, but the existence of this material has been denied by Thilo and Grunze[20] for reasons outlined in the introduction to this section. Clearly, it is desirable that structural studies be undertaken in the light of the strong evidence for the existence and stability (even if only over a limited temperature range) of a definite intermediate.

The final step in the decomposition occurs at 290 °C (cf. Boullé, et al.[19], 315 °C, and from Gallagher's[25] DTG curve, 310 °C)

$$\tfrac{1}{4}\,[K_4H_2P_4O_{13}] \rightarrow KPO_3 + H_2O \tag{4}$$

The product is, without question[14, 19], potassium (poly)metaphosphate, Kurrol's salt.

Melting of the (poly)metaphosphate occurs at about 800 °C (Osterheld and Audrieth[23] report 805 °C). Three phase transformations (at 275, 460 and 650 °C) before melting have been reported[32] for potassium (poly)metaphosphate.

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