707. *Chromium Phosphates. Part III.*[1] *Thermogravimetric, Infrared, and Magnetic Studies in the System* Cr_2O_3–P_2O_5–H_2O.

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Thermogravimetric and isothermal studies of hexa-aquochromium(III) phosphate shows that the dehydration proceeds through various complex stages. The kinetics of thermal dehydration have been investigated. The infrared spectra of the violet and a green solid phase in the system Cr_2O_3–P_2O_5–H_2O have been studied in the rock-salt region and splitting of the phosphate bands has been observed. The magnetic behaviour of some chromium(III) phosphates in the range 85—280°K shows no divergence from the Curie–Weiss law. The results are comparable with those obtained in the Cr_2O_3–As_2O_5–H_2O system.

Previous papers[1] in this series have been primarily concerned with the study of complex species of the system Cr_2O_3–P_2O_5–H_2O at 0°, 40°, and 70°. Ion-exchange studies indicated, in these solutions, the presence of polynuclear ions having structures of the type $[H_2PO_4\text{–}(Cr\text{–}HPO_4)_n\text{–}Cr\text{–}H_2PO_4]^{x+}$ where $n = 0$—3 or 6. The green solid phase isolated in the phase-diagram studies at 70° exhibited cation-exchange properties. It was concluded that the structure of this material was in some way related to the structure of the cationic polynuclear complexes present in solution. The present work is concerned with the solids in the system Cr_2O_3–P_2O_5–H_2O, in comparison with those found in the Cr_2O_3–As_2O_5–H_2O system.

Experimental

Preparation of Solids Used.—Hexa-aquochromium(III) phosphate was prepared as before.[1] The other materials used in the infrared and magnetic studies were prepared either by heating the hexa-aquo-compound to constant weight at the desired temperature or by treating appropriate amounts of the hexa-aquo-compound and phosphoric acid to give the desired Cr : PO_4 ratio in the product. The solutions were slowly evaporated at the required temperature to yield a green precipitate. Chromium and phosphate were analysed as already described.[1] Some results are given in Table 1.

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[1] Part I, Jameson and Salmon, *J.*, 1955, 360; Part II, Redfern and Salmon, *J.*, 1961, 291.

TABLE 1.

Preparations.

Material	Temp. of heating	Time of heating (hr.)	Wt. loss obs. (%)	Found Cr : PO_4 : H_2O
A	Room	—	—	1 : 1 : 6·01
B	60°	6	14·8	1 : 1 : 3·90
C	150	24	28·9	1 : 1 : 1·90
D	400	12	34·5	1 : 1 : 1·10
E	630	6	38·0	1 : 1 : 0·6
F	1000	12	42·1	1 : 1 : 0·05

Materials B—F were prepared by heating compound A to constant weight at the temperature specified.

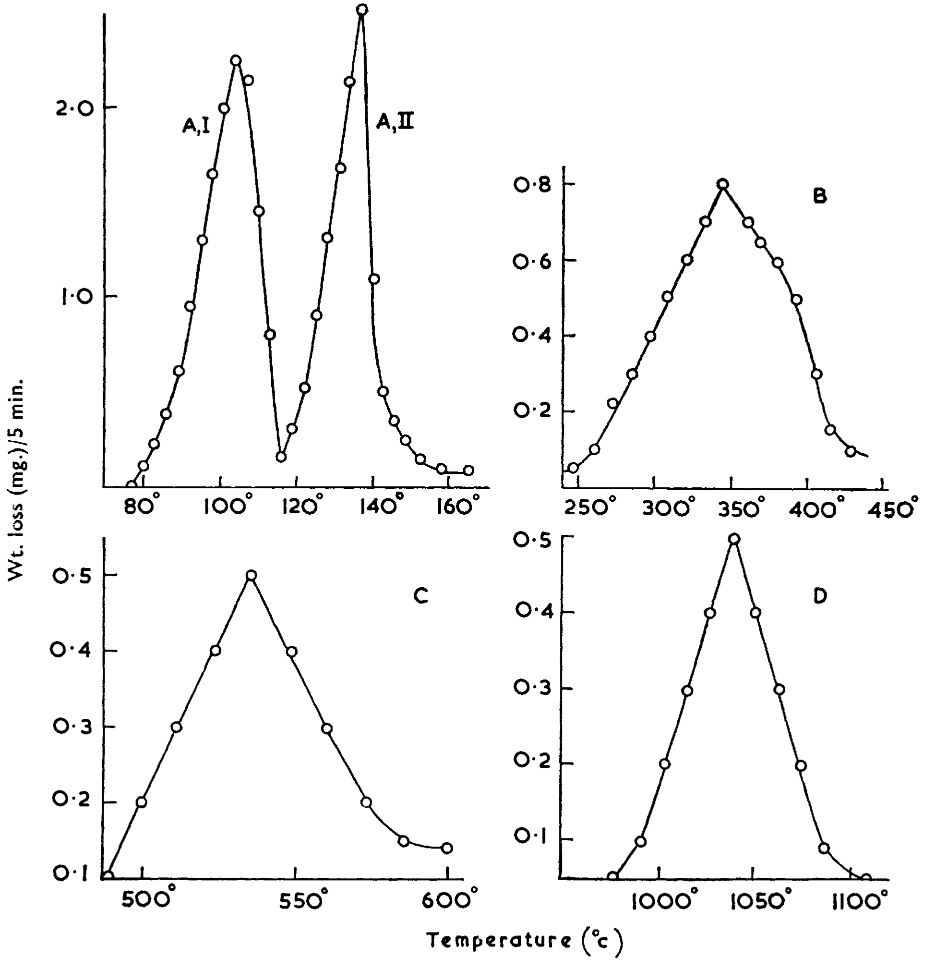

FIG. 1. Differential thermogravimetric curves of the dehydration stages of hexa-aquochromium(III) phosphate.

A, I, Reaction (1), loss at 115° is 13·6 mg., *i.e.*, 14·2%. A, II, Reaction (2), loss at 225° is 27·2 mg., *i.e.*, 28·2%. B, Reaction (3), loss at 450° is 34·0 mg., *i.e.*, 35·2%. C, Reaction (4), loss at 950° is 37·3 mg., *i.e.*, 38·6%. D, Reaction (5), loss at 1300° is 40·75 mg., *i.e.*, 42·2%. (See Table 5.)

Heating Studies.—The technique, involving use of a Stanton thermobalance (model HT-D), has been described before.[1] The results are here given for a sample weight of 96·6 mg. from 24-hr. programmes (*i.e.*, ~1° min.$^{-1}$ rise) at chart speeds of 12 in. and 3 in. per hr. Reference runs were carried out with the same platinum dish, and the necessary buoyancy corrections were applied. The total loss in weight was 42·5% [hexa-aquochromium(III) phosphate to chromium(III) phosphate requires 42·35%]. The results are given in Fig. 1. The *X*-ray powder photograph of the residue heated to 1100° was identified as that of α-chromium(III) phosphate (A.S.T.M. Index). As the sample was ground before heating, no β-phase was expected.[3]

Infrared Studies.—The technique used has been outlined previously.[2] The principal information obtained is given in Tables 2 and 3.

TABLE 2.

Infrared bands (cm.$^{-1}$) of hexa-aquochromium(III) phosphate and its thermal degradation products.

A	D′	F′	F″
715s,sp	720w,sp	—	660s,sp
750w,sp	745w,sp	740m,sp	750m,sh
—	780w,sp	785w,sh	—
860w,sh	865w,sh	870w,sh	875m,sh
900w,sh	900w,sh	925w,sh	—
950* vs,b	940* s,mb	935* s,mb	935* vs,vsp
1010w,sh	965m,sh	1025w,sh	975w,sh
—	1075m,sp	—	1090m,sp
—	1115m,sp	1125sp	—
1140w,sh	1160* s,mb	1160* s,mb	1140vs,msp
—	1250w,sh	1280w,sh	1300w,sh
1600sb	1630m,mb	—	—
1850mb	1800vw,b	—	—
~2300vw	~2300ssh,vb	~2300vw,vb	~2300vw,vb
2575 4050 } vs,vb	2540 3650 } s,vb	2550 3090 } w,b	2700vw,b

For footnotes see Table 3.

TABLE 3.

Infrared bands (cm.$^{-1}$) of material $Cr_2O_3,3P_2O_5,19H_2O$ and its thermal degradation products.

G	H	I	J
720m,sp	725w,sp	710m,sp	710m,sp
765w,sp	750w,sp	750w,sh	750m,sp
—	—	—	830s,sp
915m,sh	945w,sh	930m,sh	925,vs,sp
—	—	960s,sp	970w,sh
1060vs,mb	1030m,sh	1040m,sh	1050s,sp
—	—	1080vs,sp	1090m,sh
—	1110vs,mb	1130s,sp	1120s,sp
—	—	—	1175vs,sp
—	—	—	1250m,sh
1640m,mb	1650w,mb	1650vw,b	1650vw,b
~2300vw,vb	~2300w,vb	~2300w,vb	~2300vw,b
2570 (3390) † } vs,vb 3780	2500 (3420) † } s,vb 3675	2530 — } m,vb (3200) †	2700w,b

A = $[Cr(H_2O)_6]PO_4$; D′, F′, and F″ result from heating A to constant weight at 330°, 900°, and 1400°, respectively.

G = $Cr_2O_3,3P_2O_5,19H_2O$; H, I, and J result from heating G to constant weight at 330°, 760°, and 1100°, respectively.

sp = sharp; b = broad.

* Principal peaks in band. † Well-characterised broad peak in band approximately in the region of the given wavelength.

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[2] Lukaszewski and Redfern, *J.*, 1962, 4802.

[3] Sullivan and McMurdie, *J. Res. Nat. Bur. Stand.*, 1952, **48**, 159.

TABLE 4.

Magnetic measurements for various chromium(III) phosphate materials.

Compound A ($\theta = 5\cdot2$°K)			Compound C ($\theta = 17\cdot9$°K)			Compound F ($\theta = 35\cdot1$°K)		
μ_{eff} (B.M.)	Temp. (K)	$1/\chi'_A$	μ_{eff} (B.M.)	Temp. (K)	$1/\chi'_A$	μ_{eff} (B.M.)	Temp. (K)	$1/\chi'_A$
3·76	289·0°	164·90	3·69	299·5°	177·3	3·32	309·0°	226·4
3·79	273·8	153·30	3·66	282·0	169·8	3·30	295·8	219·6
3·73	242·0	140·10	3·68	255·3	152·0	3·35	290·1	208·1
3·71	211·3	123·60	3·66	230·2	139·0	3·29	253·0	188·5
3·71	180·5	105·70	3·64	199·5	121·6	3·26	219·7	166·7
3·71	151·0	88·35	3·63	176·8	108·2	3·23	188·0	145·4
3·71	112·0	65·54	3·59	152·5	95·5	3·15	157·0	127·5
3·71	85·5	50·00	3·49	113·0	75·9	3·09	127·7	108·0
			3·44	86·1	58·8	2·95	84·5	78·15

Magnetic Studies.—A technique similar to that described [2] before was used. The results are given in Table 4. Values of the Weiss constant θ were calculated by the method of least squares. Values of the effective magnetic moment (μ_{eff}) over the given temperature range for each material were calculated for the relation: $\mu_{\text{eff}} = 2\cdot839\sqrt{(\chi'_A T)}$, and are included in Table 4.

DISCUSSION

The dehydration of hexa-aquochromium(III) phosphate proceeds through a number of distinct stages distinguished either by plateaux or by points of inflexion in the weight loss–temperature curve. Since the final ratio of Cr : PO_4 and also the amounts of chromium and phosphate are identical with those initially present, these stages may be represented by the equations of Table 5. The kinetics of dehydration have been investigated by the method of Freeman and Carroll.[4] We use the equation

TABLE 5.

Reactions occurring in the thermal degradation of hexa-aquochromium(III) phosphate.

	Reaction	Activation energy (E^*) (kcal. mole^{-1})	Order of reaction (x)
(1)	$CrPO_4,6H_2O(s) \longrightarrow CrPO_4,4H_2O(s) + 2H_2O(g)$	45 ± 3	1·3 ± 0·3
(2)	$CrPO_4,4H_2O(s) \longrightarrow CrPO_4,2H_2O(s) + 2H_2O(g)$	66 ± 5	1·5 ± 0·3
(3)	$CrPO_4,2H_2O(s) \longrightarrow CrPO_4,H_2O(s) + H_2O(g)$	15·2 ± 1	0·5 ± 0·3
(4)	$CrPO_4, H_2O(s) \longrightarrow CrPO_4,\frac{1}{2}H_2O(s) + \frac{1}{2}H_2O(g)$	78 ± 1	3·0 ± 0·3
(5)	$CrPO_4,\frac{1}{2}H_2O(s) \longrightarrow CrPO_4(s) + \frac{1}{2}H_2O(g)$	184 ± 11	2·5 ± 0·3

$$\frac{-E^*\Delta T^{-1}/2\cdot3\boldsymbol{R}}{\Delta \log w_r} = -x + \frac{\Delta\log \mathrm{d}w/\mathrm{d}t,}{\Delta \log w_r}$$

where E^* = energy of activation of the process, $\boldsymbol{R}$ = gas constant, x = order of reaction with respect to A in the reaction $A_s \longrightarrow pB_s + qC_g$, T = absolute temperature, $w_r = (w_c - w)$, where w = weight loss at time t and w_c = weight loss at completion of the reaction. This has been shown [2] to be applicable to a single-stage irreversible process, independently of p and q and of the molecularity of the equation. Thus a plot of $(\Delta T^{-1}/\Delta\log w_r)$ against $\Delta\log(\mathrm{d}w/\mathrm{d}t)/\Delta\log w_r$ should result in a straight line of slope $-E^*/2\cdot3\boldsymbol{R}$ with an intercept of x for each stage in the dehydration.

The least-squares method was applied to the points obtained and the best lines are given for each reaction (Fig. 2). The resulting values of the orders of reaction and activation energies appear in Table 5. The results are derived from the rising portions of the dw/dt curves. The results for the first three reactions may be compared to the previously

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[4] Freeman and Carroll, *J. Phys. Chem.*, 1958, **62**, 394.

published corrected values.[5] The differences for reactions 2 and 3 are accounted for on the basis of the restrictions placed on the portions of the d*w*/d*t* curves studied. As was observed for the arsenate,[2] there is a very slow loss of residual " water " before complete dehydration. The infrared results are very similar to those found for the arsenate.[2] On dehydration of the compound a progressive weakening of the very broad absorption band occurs both in the 4000 and the 2500 cm.$^{-1}$ region. The band associated with the phosphate in the region 1250—650 cm.$^{-1}$ shows splitting and a shift towards higher frequencies (Tables 2 and 3). This behaviour may be due to the formation of the $H_2PO_4^-$ and/or HPO_4^{2-} groupings in the solid. Comparison of these values with other phosphate spectra[6] tends to support the above view. The magnetic studies show that the Curie–Weiss law is obeyed down to ~80°K and there is a progressive increase in θ as the compound is dehydrated. Since ground hexa-aquochromium(III) phosphate was used, both the magnetic and the infrared results for $CrPO_4$ relate to the α-phase. Thus the present work shows a marked similarity in the behaviour of the hexa-aquochromium(III) arsenate and phosphate:

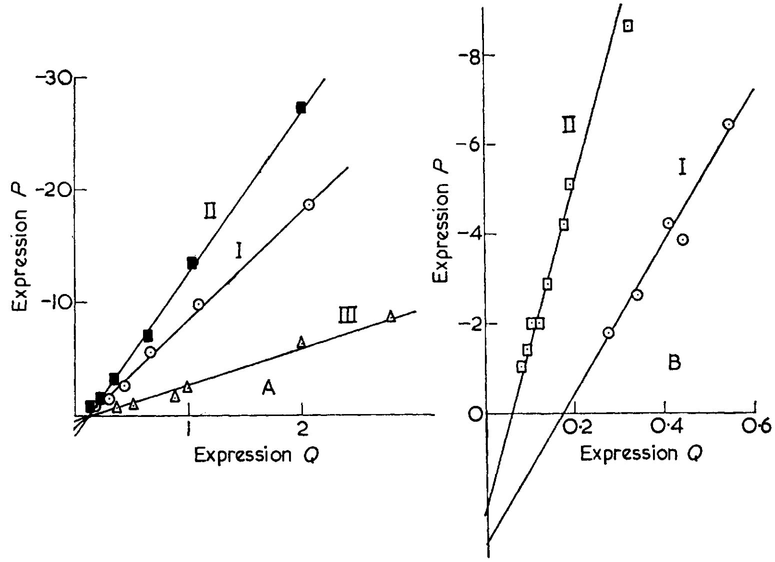

FIG. 2. Kinetics of decomposition of hexa-aquochromium(III) phosphate

$P = \Delta \log (dw/dt)/\Delta \log w_r$. $Q = 10^3 \Delta T^{-1}/\Delta \log w_r$. ($T$ is in °K.)

A, I, Reaction (1). A, II, Reaction (2). A, III, Reaction (3).
B, I, Reaction (4). B, II, Reaction (5). (See Table 5.)

(i) Similar steps were observed in the dehydration of both these compounds. The high values of E^* for reactions (1) and (2) for the phosphate (Table 4) would account for the higher stability of the hexa-aquochromium(III) phosphate. Similarly the values of E^* for reaction (5) differ, probably because α-chromium(III) phosphate is a stable phase whereas chromium(III) arsenate is not. Sullivan and McMurdie[3] carried out differential thermal analyses at a heating rate of 12½°/min. and observed a large endothermic peak

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[5] Lukaszewski and Redfern, *Nature*, 1961, **190**, 805; 1962, **193**, 223.

[6] Simon and Feher, *Z. anorg. Chem.*, 1936, **230**, 289.

at ~130° related to the loss of water and breakdown of the crystal structure. This peak appears to be complex and to possess a fine structure which is not accounted for, but is in agreement with the present thermogravimetric analyses. These workers also observed an exothermic peak around 1000° which is associated with the recrystallisation of chromium(III) phosphate without accompanying weight change.

(ii) The infrared and magnetic studies show very similar behaviour for both compounds in the course of their dehydration; the results have been interpreted in terms of the formation and subsequent decomposition of polymeric species involving anion or hydroxide bridging but excluding oxygen bridging.[1] Similarly, partially dehydrated solids in both cases possess ion-exchange properties.

(iii) Both the partially dehydrated phosphate and arsenate materials fail to show any characteristic *X*-ray pattern—such a pattern occurring only on recrystallisation of the chromium phosphate around 950—1000°. However, these materials do yield patterns consisting of two or three very diffuse maxima, suggesting the existence of a certain measure of order in the structures. A more detailed *X*-ray examination is being undertaken [7] to determine the relation between the crystalline and the amorphous phase. The above observations are in accord with all the chemical evidence so far presented and also with the work of Shafer and Roy [8] who found the products of dehydration of hexa-aquochromium(III) phosphate at 200° to be amorphous to *X*-rays, whereas electron diffraction yielded a definite diffraction pattern, the shorter wavelength of this radiation revealing a degree of crystallinity not detectable by the longer wavelength of the *X*-rays. These workers crystallised the " amorphous " material obtained at 200° by hydrothermal treatment under a pressure of 25,000 lb./in.^{2}, obtaining a compound designated $CrPO_4,\frac{1}{2}H_2O$ which yielded an *X*-ray powder pattern with *d*-spacings comparable with that of the " amorphous " phase; it is related to the hexa-aquo-compound and both the α- and the β-chromium phosphate phase.

These results therefore seem to establish the polymeric and disordered nature of the intermediate materials obtained in the dehydration of both the hexa-aquoarsenate and -phosphate.

Thus the early reactions indicated in Table 5 are stages in a process of olation-condensation occurring in the hexa-aquo-compound. The final stages of dehydration are represented by a depolymerisation in the solid. These stages are associated with an absorption of heat, and the differential thermal analytical results of Sullivan and McMurdie [3] are in accord with this, while the final recrystallisation yielding a stable lattice of lower energy is exothermic.

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[7] Lukaszewski and O'Donnell, personal communication.

[8] Shafer and Roy, *J. Amer. Chem. Soc.*, 1956, **78**, 1087.