

CHARACTERIZATION OF SODIUM AND POTASSIUM POLYCHROMIUM(III) PHOSPHATES IN SOLID-STATE REACTIONS AT 400–420°C

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ABSTRACT

Solid-state reactions of equimolar ratios of $K_2Cr_2O_7$ with (I) $K_3PO_4 \cdot 3 H_2O$, (II) $Na_5P_3O_{10}$ and (III) $Na_3P_3O_9$ were carried out at 400–420°C. Green, water-insoluble products in the three systems were isolated and investigated by chemical analysis, X-ray diffraction, electronic and IR vibrational spectra measurements. Moreover, a DTA curve of the $K_2Cr_2O_7$ – $Na_3P_3O_9$ system(III) was recorded, and X-ray diffractograms of differently annealed green products were measured. Crystalline phases with formula $K_6Cr_2P_6O_{21}$ in the orthophosphate(I), $Na_2KCr_2P_3O_{12}$ in the tripolyphosphate(II) and $Na_4K_2Cr_2P_6O_{21}$ in the trimetaphosphate(III) systems were identified. Assignments of IR spectra revealed the presence of $(P_2O_7)^{4-}$ and $(PO_4)^{3-}$ structural units in the polyphosphate $(P_6O_{21})^{12-}$ and $(P_3O_{12})^{9-}$ groups, respectively. The measured electronic absorption spectra of the solid powders were characteristic of hexacoordinated Cr(III). The results were discussed in comparison with previous work.

INTRODUCTION

Many reactions in different Cr(III)–phosphate systems (solids or solutions) are well known [1–4] in comparison with those of Cr(VI). A polymerisation process seemed to take place in such reactions leading to the formation of poly Cr(III) phosphates, the constitution of which depends greatly on the experimental conditions. In previous work [4], $(PO_4)_3^{9-}$ and $(PO_4)_4^{12-}$ polyions were detected in solid mixtures of Cr_2O_3 – MH_2PO_4 ($M = Na^+$, NH_4^+) reacting at the two different high temperatures of 900 and 1300°C. On the other hand, $(P_2O_7)^{4-}$ structural units were found to be formed on melting an orthophosphate mixture (20% $AlPO_4$ + 80% KH_2PO_4) at a temperature of 1100°C [5].

Recently, similar units of $(P_2O_7)_3^{12-}$ and $(PO_4)_3^{9-}$ were characterized in solid-state reaction products obtained at 400–420°C in the $K_2Cr_2O_7$ – $K_4P_2O_7$ and $K_2Cr_2O_7$ – $NaPO_3$ (glass) systems, respectively [6]. In general, it could be seen from the reported results that the type of phosphate ions used (as one of the experimental factors) contributes greatly to the structure of the

resulting polymerised phosphates. Moreover, the temperature of formation of such poly Cr(III) phosphates seems to depend greatly on the nature of the second reactant, whether calcined Cr_2O_3 or $\text{K}_2\text{Cr}_2\text{O}_7$. Thus, this work aims to investigate, furthermore, the behaviour of some simple ($\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$) and condensed ($\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{Na}_3\text{P}_3\text{O}_9$) phosphates towards $\text{K}_2\text{Cr}_2\text{O}_7$ at a temperature near its melting point.

EXPERIMENTAL

The preparation of the reacting mixtures at equimolar ratios, thermal treatment and isolation of the insoluble parts were the same as reported previously [6]. The isolated green phase in the $\text{K}_2\text{Cr}_2\text{O}_7\text{-Na}_5\text{P}_3\text{O}_{10}$ system was crystalline, whereas the crystallinity of those phases isolated in the other two systems, $\text{K}_2\text{Cr}_2\text{O}_7\text{-K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7\text{-Na}_3\text{P}_3\text{O}_9$, was achieved by further annealing at 400–420°C for 18 and 256 h, respectively. The three crystalline phases were then chemically analysed. A Philips X-ray diffractometer, and Perkin-Elmer 577 (KBr disc method) and automatic Carl Zeiss DMR21IR spectrophotometers were used in the measurements. DTA curves were obtained using a Shimadzu apparatus at a heating rate of $10^\circ\text{C min}^{-1}$, sensitivity $10 \mu\text{V in.}^{-1}$ and air flow 30 ml min^{-1} . $\text{K}_2\text{Cr}_2\text{O}_7$ (PA) and $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (Purest) were Merck products. $\text{Na}_5\text{P}_3\text{O}_{10}$ and $\text{Na}_3\text{P}_3\text{O}_9$ were kindly provided by Prof. E. Thilo (Berlin).

RESULTS AND DISCUSSION

DTA curves are shown in Fig. 1, and Fig. 2 shows the effect of annealing some green products on their corresponding X-ray diffraction patterns. Figures 3 and 4 show the electronic and IR vibrational spectra, respectively. Table 1 gives the assignments of IR vibrational frequencies. According to chemical analyses, the formulae of the isolated green phases in the $\text{K}_2\text{Cr}_2\text{O}_7\text{-K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{Cr}_2\text{O}_7\text{-Na}_5\text{P}_3\text{O}_{10}$ systems can be given as $\text{K}_6\text{Cr}_2\text{P}_6\text{O}_{21}$ and $\text{Na}_2\text{KCr}_2\text{P}_3\text{O}_{12}$, respectively. Their elemental analysis is

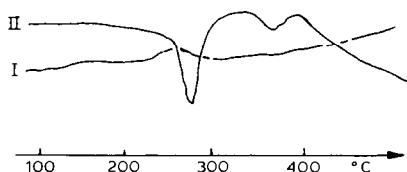


Fig. 1. DTA of (I) $\text{Na}_3\text{P}_3\text{O}_9$ and (II) $\text{K}_2\text{Cr}_2\text{O}_7\text{-Na}_3\text{P}_3\text{O}_9$ (1:1 molar ratio) at a heating rate of $10^\circ\text{C min}^{-1}$.

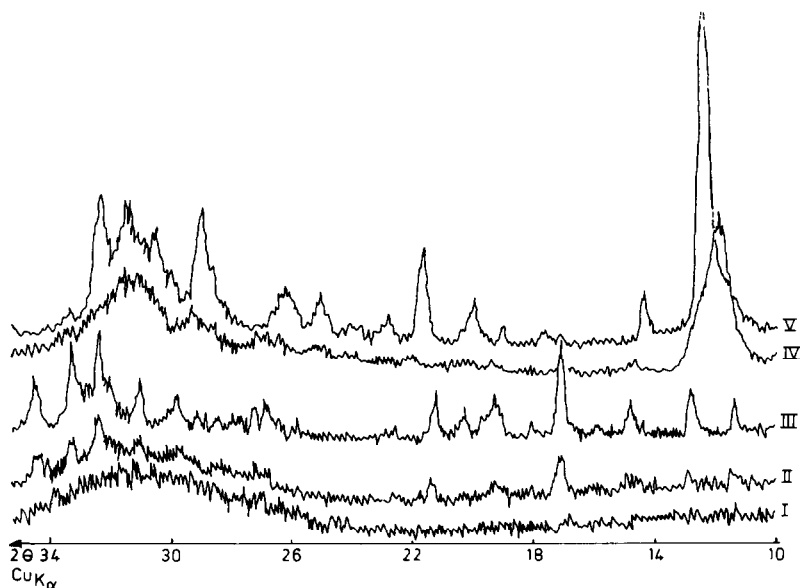


Fig. 2. X-ray diffraction patterns of isolated green reaction products in systems $\text{K}_2\text{Cr}_2\text{O}_7\text{-Na}_3\text{P}_3\text{O}_9$ (I, II, III) and $\text{K}_2\text{Cr}_2\text{O}_7\text{-K}_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ (IV, V) differently heated at $400\text{-}420^\circ\text{C}$. (I) Unheated, (II) 66 h, (III) 256 h, (IV) unheated, (V) 18 h (curves II-V are shifted towards coordinate).

practically the same as those identified previously in the $\text{K}_2\text{Cr}_2\text{O}_7\text{-K}_4\text{P}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7\text{-NaPO}_3$ systems [6]. On the other hand, chemical analysis of the isolated green phase in the $\text{K}_2\text{Cr}_2\text{O}_7\text{-Na}_3\text{P}_3\text{O}_9$ system suggests the formula $\text{Na}_4\text{K}_2\text{Cr}_2\text{P}_6\text{O}_{21}$ (found (%): Na, 12.84; K, 9.77; Cr, 13.8; P, 22.53; theor. (%): Na, 12.0; K, 10.00; Cr, 13.0; P, 23.0).

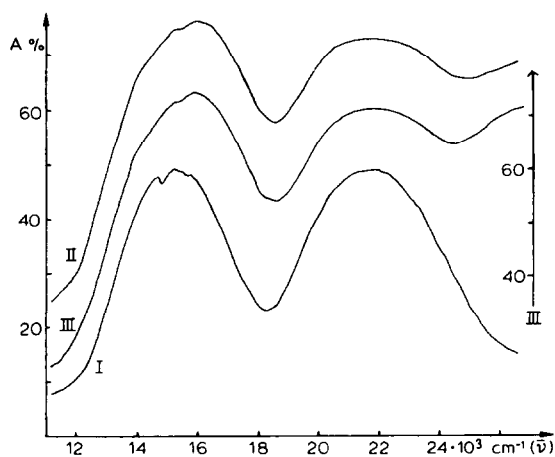


Fig. 3. Electronic absorption spectra of (I) $\text{K}_6\text{Cr}_2\text{P}_6\text{O}_{21}$, (II) $\text{Na}_2\text{KCr}_2\text{P}_3\text{O}_{12}$ and (III) $\text{Na}_4\text{K}_2\text{Cr}_2\text{P}_6\text{O}_{21}$.

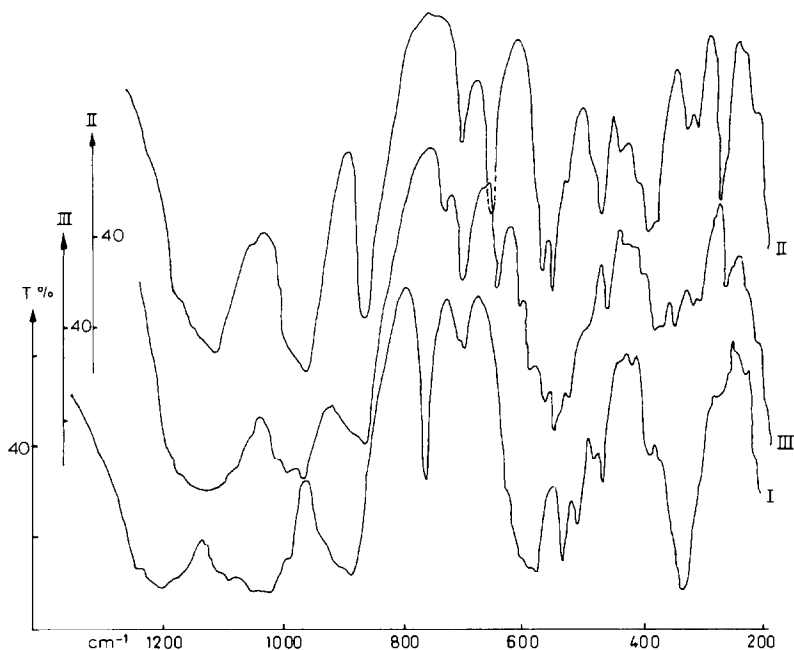
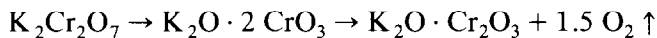


Fig. 4. IR vibrational spectra of (I) $K_6Cr_2(P_2O_7)_3$, (II) $Na_2KCr_2(PO_4)_3$ and (III) $Na_4K_2Cr_2(P_2O_7)_3$.

DTA and effect of annealing on crystallinity

The measured DTA curve of $K_2Cr_2O_7-Na_3P_3O_9$ (Fig. 1, curve II) shows two endothermic peaks of different intensities at 280 and 365°C together with two broad exothermic peaks of weak intensity at 300–345 and 390°C. The first strong endothermic peak at 280°C may be attributed to a dissociation process of $K_2Cr_2O_7$ with evolution of oxygen, probably in the following manner



The actively formed Cr_2O_3 reacts simultaneously with the $Na_3P_3O_9$ present leading to an intermediate Cr(III)-phosphate compound, the formation of which is accompanied by the first exothermic peak at 300–345°C. On raising the temperature, the assumed intermediate compound undergoes a second dissociation process which is illustrated by the second endothermic peak at 365°C.

The last exothermic peak at 390°C could be related to the formation of a Cr(III)-phosphate phase which seems to be stable under the present experimental conditions. This general thermal behaviour of $K_2Cr_2O_7$ towards alkali phosphates concerning its early dissociation at 280°C ($K_2Cr_2O_7$ -dissociation occurs at $\geq 450^\circ C$) and formation of intermediate unstable compounds is in fair agreement with that already found in the case of the $K_2Cr_2O_7-MoO_3$ system [7].

Regarding the crystallinity of the isolated green products, it was found that the phase obtained in the $\text{Na}_5\text{P}_3\text{O}_{10}$ (II) system was crystalline, whereas those in the $\text{K}_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ (I) and $\text{Na}_3\text{P}_3\text{O}_9$ (III) systems were amorphous. On further annealing of the amorphous phases for different periods at 400–420°C, their crystallization was achieved (Fig. 2). It is, however, remarkable that in the case of the $\text{Na}_3\text{P}_3\text{O}_9$ (III) system, the crystallinity of the green product was reached after a relatively long time (256 h) in comparison to that in the case of the $\text{K}_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ (I) system.

The different structures of $\text{K}_3\text{PO}_4 \cdot 3 \text{H}_2\text{O}$ (isolated) and $\text{Na}_3\text{P}_3\text{O}_9$ (ring) could be the cause of such an obvious difference in heating periods since the ring structure might undergo an additional cleavage process. Moreover, a slight difference can be observed between the X-ray diffraction patterns of the $\text{Na}_4\text{K}_2\text{Cr}_2\text{P}_6\text{O}_{21}$ and $\text{K}_6\text{Cr}_2\text{P}_6\text{O}_{21}$ crystalline phases (Fig. 2, curves III and V, respectively) which could be related to a probable difference in their crystal structure.

Electronic absorption spectra

The spectra (Fig. 3) show two strong spin-allowed absorption bands with their maxima centred at 15 500–15 900 (I) and 21 800–21 900 cm^{-1} (II) which are characteristic of Cr(III) in an octahedral coordination. The two bands are assignable to: ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (I) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (II) within the energy level diagram of Cr^{3+} ($3d^3$).

Moreover, a shoulder appears at $15\,000 \pm 250 \text{ cm}^{-1}$ on the descending branch of the low-frequency band towards the IR region. This result suggests that Cr(VI) as starting valency undergoes a reduction process under the loss of oxygen, in agreement with previous similar reactions [6,7]. The value of the ligand field energy, Δ (band I), is lower than that of the Cr(III)–aquo complex ($\Delta = 17\,200 \text{ cm}^{-1}$) [8] by about 7.65–10%.

The remarkably low value of Δ can be attributed to a contracting polarisation effect of P(V) and, hence, a weakness of the Cr–O bond strength, in agreement with results previously reported on many P(V)-containing compounds [6,9,10]. The calculated values of the nephelauxetic ratio, β (B/B_0), for the three phases lie between 0.66 and 0.77 indicating that the Cr–O bond is of covalent character. However, π -bonding contributions increase with increasing β .

IR spectra

The present IR vibrational frequencies (Table 1, Fig. 4) are assigned on the basis of previous results on alkali ortho-, pyro- and poly Cr(III) phosphates [6,11,13]. It can generally be seen that two types of structural units, $(\text{P}_2\text{O}_7)^{4-}$ and $(\text{PO}_4)^{3-}$, are present. According to this characterization, the isolated phases in tripoly-, ortho- and trimetaphosphate systems can be

TABLE 1

Assignments of vibrational frequencies (cm^{-1}) of isolated green phases in potassium dichromate-ortho- (I), trimeta- (II), and tripolyphosphate (III) systems

$(\text{P}_2\text{O}_7)^{4-}$ [10]	I $(\text{K}_6\text{Cr}_2(\text{P}_2\text{O}_7)_3)$	II $(\text{Na}_4\text{K}_2\text{Cr}_2(\text{P}_2\text{O}_7)_3)$	Assign. $(\text{PO}_4)^{3-}$ [11]	III $(\text{Na}_2\text{KCr}_2(\text{PO}_4)_3)$	Assign.
	265 sh			280 sh	
	275 sh	290 w		288 st	
	305 sh			330 w	
334	335 st	330 w	δPOP	345 w	
				390 m	
	390 sh	340 w		410 m	$\nu\text{OPO b. (E)}$
		370 m	461	430 sh	
		392 m		460 w	
				485 st	
425 ^a	418 sh	408 m			
470	468 m	460 sh	$\delta_3\text{PO}_3$	540 sh	$\nu\text{OPO b. (F}_2)$
	482 w	485 m		562 st	
	508 w	520 sh		572 st	
				590	
				668 st	

600	535 m 575 st	540 w 565 m 582 w 608 w	$\delta_{as} PO_3$	720 m	
	625 sh			875 st	A_1
730	695 m 700 sh		$\nu_3 POP$	970 st 990 sh	$\nu_s PO_3$
915	760 st 882 st 930 sh	760 w 880 m 900 sh	$\nu_{as} POP$	1120 st, br 1190 sh	$\nu_{as} PO_3$
986	982 sh	970 w	$\nu_s PO_3$		} F_2
1024	1025 m, br	1008 w 1025 w			
1122	1090 sh	1065 sh	$\nu_{as} PO_3$		
1135	1115 sh	1130 m, br			
1150	1200 m, br	1190 sh			

^a This work. st = strong, m = medium, w = weak, br = broad, sh = shoulder.

safely formulated as $\text{Na}_2\text{KCr}_2(\text{PO}_4)_3$, $\text{K}_6\text{Cr}_2(\text{P}_2\text{O}_7)_3$ and $\text{Na}_4\text{K}_2\text{Cr}_2(\text{P}_2\text{O}_7)_3$, respectively. From the symmetry point of view, it is known that tetrahedrally free $(\text{PO}_4)^{3-}$ ions with T_d site-symmetry have only two IR-active bands [$F_2(\nu_3$ and $\nu_4)$].

On lowering the site-symmetry of the free ions in crystals, the spectra will show more bands due to splitting of degenerate vibrations and partial removal of ν_1 and ν_2 (A_1 and E modes) prohibition. In fact, there is an increase in the number of IR vibrational frequencies (Table 1), which may be attributed to such a lowering of site-symmetry.

This conclusion is in fair agreement with many results reported earlier [12,14]. Moreover, a splitting of some P–O vibrations and hence some more bands are observed on partial substitution of K^+ by Na^+ ions in the $\text{K}_6\text{Cr}_2(\text{P}_2\text{O}_7)_3$ phase (Table 1 and Fig. 4). Apart from the correlated P–O frequencies of PO_3 and P–O–P groups, the spectra show additional bands in the regions of O–P–O, P–O–P and symmetrical PO_3 bending vibrations (Table 1). Such bands may be related to the bending of metal–oxygen bonds and Cr–O stretching vibrations. Steger and Leukroth [15] assigned frequencies in the region of 402 and 425 cm^{-1} to metal–oxygen bending vibrations in cubic diphosphates, whereas the range 445–525 cm^{-1} was ascribed to Cr–O stretching vibrations [16]. However, some relatively strong bands appear in the spectra at 392, 410 and 485 ($\text{Na}_4\text{KCr}_2(\text{PO}_4)_3$), 335, 468 ($\text{K}_6\text{Cr}_2(\text{P}_2\text{O}_7)_3$) and 370, 390, 408, 485 cm^{-1} ($\text{Na}_4\text{K}_2\text{Cr}_2(\text{P}_2\text{O}_7)_3$). The increase in intensity may be due to the coupling of some Cr–O vibrations with those of P–O–P bending and symmetrical PO_3 vibrations in $(\text{P}_2\text{O}_7)^{4-}$ groups, O–P–O bending in $(\text{PO}_4)^{3-}$ units (E mode) and metal–oxygen bending vibrations.

The IR range assigned to Cr–O stretching vibrations in the present work lies below $\nu \approx 520 \text{ cm}^{-1}$, which is different from that of connected CrO_6 octahedra in known structures such as Cr_2O_3 and MgCr_2O_4 . The IR range 440–680 cm^{-1} was found to be specific to Cr(III) in both the above-mentioned structures [17,18], whereas McDevitt and Baun [19] reported another IR range (407–625 cm^{-1}) for Cr_2O_3 . The absence of any higher frequencies which could be related to Cr–O stretching vibrations may suggest that CrO_6 -octahedra are isolated in the phases under investigation, in analogy with ZrO_6 -octahedra in a similarly known $\text{NaZr}_2\text{P}_3\text{O}_{12}$ compound [20].

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