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A STUDY OF THERMAL PREPARATION OF c-$Mn_2P_4O_{12}$

D. Brandová and *M. Trojan*

DEPARTMENT OF INORGANIC TECHNOLOGY, INSTITUTE OF CHEMICAL TECHNOLOGY, 53210 PARDUBICE, CZECHOSLOVAKIA

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With the application of thermogravimetry under quasi-isothermal-isobaric conditions, the reaction course of the calcination of $Mn(H_2PO_4)_2 \cdot H_2O$ to give dimanganese cyclotetraphosphate has been studied. Isothermal calcination was also carried out in an electric furnace at various temperatures (200 min). The reaction products were analyzed by chromatography, IR and NMR spectrocopy, and X-ray diffraction analysis. The compositions of the calcinates were determined through extraction with various inorganic and organic solvents.

Condensed phosphate of some bivalent metals have recently acquired considerable significance. Their application as microelement fertilizers with long-term activity and, in some cases, also as special thermostable pigments [1, 2] has been suggested. However, the reaction mechanism of their formation is not fully understood, and the respective reaction conditions too need to be specified in more detail. Of the condensed phosphates, the cyclo-tetraphosphates seem to be the most suitable for the above purposes. They can be prepared by calcination of the dihydrogen phosphate [3–6] or mixtures containing phosphorus and the bivalent metal in the corresponding ratio [3, 5].

One of the cyclo-tetraphosphates possessing suitable properties is c-$Mn_2P_4O_{12}$. Available papers [3–6] dealing with its preparation do not give exact data on the calcination temperatures necessary for the condensation reactions to take place; nor do they present a uniform view of the reaction mechanism, and they neglect the effect of the water vapour pressure, which is an important factor in the course of the condensation reactions.

From a consideration of the results [7, 8] on the thermal decomposition of $MnNH_4PO_4 \cdot H_2O$, $CoNH_4PO_4 \cdot H_2O$, $CdNH_4PO_4$ and Ca^{2+} and Mg^{2+} hydrogen phosphates [9], obtained through thermogravimetry under quasi-isothermal-isobaric conditions, we presumed that the same experimental method could provide data on the thermal decomposition of $Mn(H_2PO_4)_2 \cdot H_2O$, necessary to complete our ideas about the condensation reaction course. The present communication gives an account of our experimental results on the above reaction.

Experimental

Pure $Mn(HPO_4)_2 \cdot 2H_2O$ with the ratio $MnO/P_2O_5 = 0.9998$ was prepared as a light-pink crystalline solid; its purity was checked by X-ray diffraction analysis. The substance was examined by thermogravimetry (Q–TG) under quasi-isothermal-isobaric conditions [10] (Q-1500 derivatograph, Hungarian Optical Works, MOM, Budapest, Paulik–Paulik–Erdey System). The decomposition rate chosen was 0.4 mg/min (calculated for 200 mg total weight change). The weighed amount of sample: 800 mg. Sensitivity of the balance: 200 mg. Temperature range: 20–500°. Atmosphere: air.

Various platinum crucibles (Fig. 1) were used for the measurements [10]: a multiplate crucible (A), an open crucible (B), a crucible with a lid (C), and a six-component labyrinth set (D). The last arrangement (D) allows retention of the water vapor released during the calcination of dihydrogen phosphate, so that its partial pressure is maintained at about 100 kPa (quasi-isobaric conditions) [10]. In cases (A), (B) and (C) the partial pressures correspond approximately to 1 kPa (which is negligible), 5 kPa, and 20 kPa, respectively.

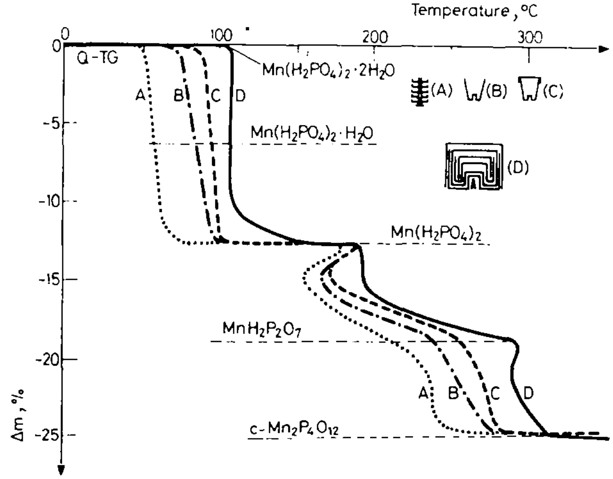

Fig. 1 TG curves of $Mn(H_2PO_4)_2 \cdot 2H_2O$ recorded under quasi-isothermal-quasi-isobaric conditions. Sample weight: 800 mg, decomposition rate: 0.2 mg · min^{-1}

The results obtained from these thermal analyses were then made use of in preparation of the condensation products and intermediates by calcination of the starting dihydrogen phosphate in an electric furnace at various temperatures (60, 80, 100, 120, . . . , 300°), the isothermal conditions in crucible (B) or (D) being maintained for 200 min.

On the basis of the results of our earlier investigations [11], various organic (acetone, butanone) and inorganic solvents (dilute hydrochloric acid) [2] were chosen for extraction of the calcinates. The extraction experiments made it possible to follow the formation and existence of the individual intermediates, particularly dihydrogen diphosphate. The samples prepared by calcination in the electric furnace under isothermal conditions were extracted with acetone (Fig. 2). The extractable phosphate components (phosphoric or diphosphoric acid), expressed as the P_2O_5 fraction of the total content of the calcinate, are given by curves 3 and 6 for crucibles (B) and (D), respectively. Thereafter, the calcinates were extracted with water (curves 1 and 4), which dissolves the intermediate $MnH_2P_2O_7$ formed. The samples calcined above 120° were extracted with 0.3 M HCl (curves 2 and 5), in which only the final product c-$Mn_2P_4O_{12}$ is insoluble. As already shown [2], these extraction experiments make it possible to follow the degree of conversion of $Mn(H_2PO_4)_2 \cdot 2\,H_2O$ into c-$Mn_2P_4O_{12}$).

The calcinates were analyzed and the individual products prepared in the thermal analysis under quasi-isothernal-isobaric conditions [10] were identified by means of TLC [12], IR spectroscopy [13] (Perkin–Elmer 684 infrared spectrometer), X-ray diffraction analysis [5] (an HZG-4 apparatus, DDR) and NMR spectroscopy (Jeol JNM-Fx 100). The solid residues from each extraction experiment were analyzed by the above instrumental methods too. On boiling with dilute (1 : 1) hydrochloric acid, the residues were dissolved, and the MnO/P_2O_5 ratios were determined by atomic absorption spectrometry.

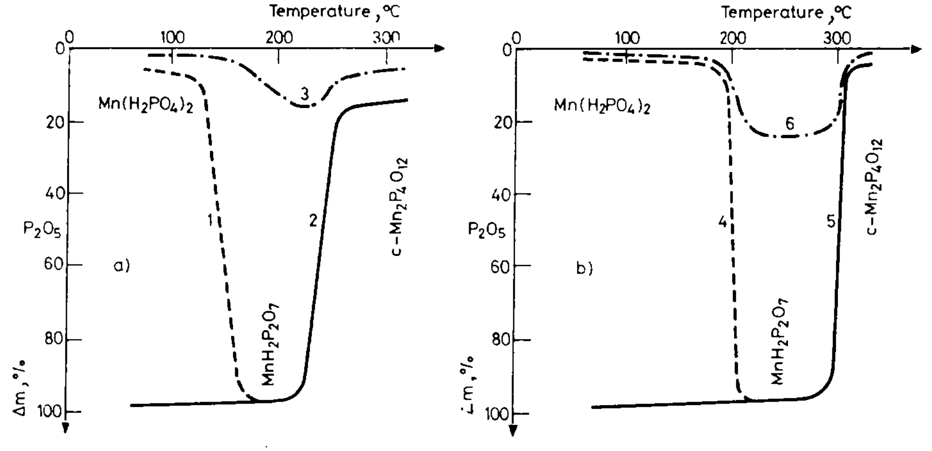

Fig. 2 Extraction experiments on $Mn(H_2PO_4)_2 \cdot 2\,H_2O$ calcinates obtained in an open crucible (a), or in a labyrinth arrangement (b). Weight changes of the intermediates determined by extraction with water (curves 1 and 4), or with 0.3 *M* HCl (curves 2 and 5), and the P_2O_5 portion extracted with acetone (curves 3 and 6)

Results and discussion

The thermogravimetric curves (Q–TG) recorded under quasi-isothermal-isobaric conditions (Fig. 1) indicate the splitting-off of both molecules of crystal water from

$Mn(H_2PO_4)_2 \cdot 2H_2O$ in the first step (weight loss 12.6%), the following temperature intervals being found for the individual crucibles: (A) 60–76°, (B) 80–100°, (C) 100–110° and (D) 120°. This means that the temperature of the escape of crystal water decreases with increasing partial pressure of the water vapour above the analyzed sample. It is also evident from the Q–TG curves that this reaction proceeded practically isothermally. From what has been said [10], it follows that this reaction leads to equilibrium.

The existence of anhydrous $Mn(H_2PO_4)_2$ in the temperature interval from 150° to 190° was confirmed from the IR spectra and by X ray diffraction analysis of its crystalline character.

The constitution water is released at bout the same temperature in all types of crucibles used, viz. at 190°. Thereafter, the temperature of the samples in crucibles (A), (B) and (C) decreases spontaneously to 155°, 165° and 175°, respectively, due to the splitting-off of $1/2\ H_2O$. This phenomenon can be explained as follows: the formation of nuclei initiating the transformation takes place at higher temperature (i.e. higher energy content) in this case. As soon as a sufficient number of these nuclei are formed, the temperature decreases to the value corresponding to the actual partial pressure of water vapour. In crucible (D) this splitting-off of the first $1/2\ H_2O$ proceeds at constant temperature. In this case the temperature decrease is not observed, since the conversion takes place at 100 kPa partial pressure of water vapour and with a preselected rate at 190°. During the escape of the second half of the water molecule, the temperature increases by 50–100°. This fact can be explained, however, on the basis of numerous earlier findings [11]. It can be supposed that the porosity of the crust covering the grains is low in this case. The escape of water through the pores therefore becomes increasingly more difficult, which results in the continuous increase of the temperature of the transformation. In the individual types of the crucibles used, this process is completed at different temperatures: (A) 215°, (B) 250°, (C) 265° and (D) 285°. Consequently, the Q–TG curves show inflexion points at the mass loss corresponding to $MnH_2P_2O_7$.

The existence of $MnH_2P_2O_7$ was confirmed by means of TLC and IR spectroscopy (the presence of absorption bands corresponding to valence vibrations of dihydrogen phosphate [13]). The amorphous (glassy) character of the intermediate $MnH_2P_2O_7$ formed within the given temperature interval was confirmed by X-ray diffraction analysis and electron microscopy, which proved a certain degree of porosity of this intermediate (this degree probably depends on the pressure of water vapour).

The intermediate (which was also prepared by calcination of the strating sample in the above-mentioned way under isothermal conditions) was subjected to extraction experiments. The evaluation (Fig. 2) indicated that a part of the phosphate component is split off, either in the form of phosphoric acid from the intermediate anhydrous dihydrogen phosphate, or in the form of diphosphoric acid from the first condensation product, dihydrogen diphosphate. Figure 2 (curves 3 and 6) shows a distinct region of enhanced extractability of P_2O_5 by acetone from the calcinates prepared in crucible (B) at 170–240° and in (D) at 205–300°. These regions correspond to the formation and existence of the first condensation product, $MnH_2P_2O_7$. The phosphate component is extracted partially with acetone from this intermediate [2] which, at the same time, is transformed partially into the normal diphosphate, $Mn_2P_2O_7$ (the ratio MnO/P_2O_5 found approaches 2). The released acid condenses independently (the reaction temperature of this process is lower at the beginning), so that the condensation reaction also proceeds at the temporarily reduced temperature of the sample. With further gradual increase of temperature, polyphosphoric acids of higher condensation degree are formed. Both chromatography and NMR spectroscopy could prove only the presence of diphosphate ions in the calcinate and in the acetone-extracted residue, and IR spectroscopy showed absorption bands corresponding to diphosphate and dihydrogen diphosphate. From Fig. 2 it is obvious that these results confirm the presumed effect of the water vapour pressure on the formation of the side-intermediates, which affects the overall reaction yield.

The temperatures at which the last of the water is released from the calcined sample, i.e. the second molecule of the constitution water of the starting dihydrogen phosphate, and which correspond to the second condensation reaction, i.e. formation of c-$Mn_2P_4O_7$, again depend on the type of crucible employed, i.e. on the partial pressure of water vapour between the grains of the sample. At the same time, however, it was found that this transformation did not exhibit an isothermal course, occurring within fairly wide temperature intervals: (A) 220–265°, (B) 250–295°, (C) 270–300° and (D) 320–339°. These results allow the conclusion that the decomposition reaction leads to equilibrium. This conclusion, however, disagrees with the loss of the second molecule of constitution water. Considering all the circumstances, we can conclude that the reaction probably leads to equilibrium, but that its course is affected by the different degrees of porosity of the crust formed on the grains. With crucible (D) the total mass loss is 25.4%, and it does not change further with increasing temperature. This fact agrees well with the theoretical value of 25.29% corresponding to the total release of four water molecules from the starting $Mn(H_2PO_4)_2 \cdot 2\,H_2O$. In the remaining types of crucibles, where there was a partial release and independent condensation of phosphoric acid in the first condensation reaction of $MnH_2P_2O_7$ formation, such a mass loss (25.29%) was not reached up to 380°. The reason is that both the condensation of the released phosphoric acid to higher condensation degrees and the partial formation of $Mn_2P_2O_7$ are shifted to higher temperatures, i.e. above the temperature of formation of c-$Mn_2P_4O_{12}$ [2]. The final degree of conversion of the calcinate into cyclo-tetraphosphate is also distinctly lower (85%) in the open crucible (B). The given final conversion degrees of the calcinates into cyclo-tetraphosphate were confirmed by extraction experiments (with 0.3 *M* HCl) of the samples calcined in electric furnaces (Fig. 2, curves 2 and 5) [2].

At calcination temperatures above 265°, the maximum degree of transformation into cyclo-tetraphosphate was 80% in the open crucible (curve 2 in Fig. 2); in the labyrinth system (D) the conversion degree was higher than 95% at temperatures above 310° (curve 5). From the extraction experiments (Fig. 2) it follows that cyclo-tetraphosphate begins to appear in the calcinates prepared in electric furnaces from

210° in the open crucible (curve 2) and from 290° in the labyrinth system (curve 5): the acetone-extractable portion of the samples decreases proportionally (curves 3 and 6). c-$Mn_2P_4O_7$ is the main condensation product in the open crucible above 260°, and practically the only product in the labyrinth crucible above 310°: this product resists even the action of 0.3 *M* HCl, and the ratio of its components is $MnO/P_2O_5 = 1$. Its existence was confirmed by the methods of instrumental analysis [11–13]. Our results disagree partially with those of authors [5, 6] who used different methods and found different temperatures and also detected linear manganese(II) tri- and tetraphosphates as intermediates.

Conclusion

The above investigation of the effect of the presence of water vapour on the course of the condensation reactions during the calcination of $Mn(H_2PO_4)_2 \cdot 2\,H_2O$ indicates that the individual reactions taking place under a water vapour partial pressure of 100 kPa can be represented by the following scheme:

$$Mn(H_2PO_4)_2 \cdot 2\,H_2O \xrightarrow[-2\,H_2O]{120^\circ} Mn(H_2PO_4)_2 \xrightarrow[-H_2O]{205-210^\circ} MnH_2P_2O_7$$

$$2\,MnH_2P_2O_7 \xrightarrow[-2\,H_2O]{310-320^\circ} \text{c-}Mn_2P_4O_{12}$$

At lower vapour pressure the reaction proceeds at temperatures lower by 40–70°, the yield of the final c-$Mn_2P_4O_{12}$, however, also being lower. Besides the main intermediate (i.e. $MnH_2P_2O_7$), further products are also found due to the release of part of the phosphate component in the form of phosphoric or diphosphoric acids, which are condensed to higher polyphosphoric acids. The excess of the manganese(II) component thus obtained is compensated by the formation of $Mn_2P_2O_7$. Formation of these intermediates decreases the yield of the final c-$Mn_2P_4O_{12}$.

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Zusammenfassung — Der Verlauf der Dimangan-cyclotetraphosphat ergebenden Kalzinierung von $Mn(H_2PO_4)_2 \cdot H_2O$ wurde thermogravimetrisch unter quasi-isothermen-isobaren Bedingungen untersucht. Isotherme Kalzinierung wurde auch im elektrischen Ofen (200 min) bei verschiedenen Temperaturen ausgeführt. Die Reaktionsprodukte wurden chromatographisch, IR- und NMR-spektroskopisch sowie röntgendiffraktometrisch analysiert. Die Zusammensetzung der kalzinierten Produkte wurde via Extraktion mit verschiedenen anorganischen und organischen Lösungsmitteln bestimmt.

Резюме — Термогравиметрическим методом в квазиизотермических и квазиизобарных условиях изучена реакция прокаливания соединения $Mn(H_2PO_4)_2 \cdot H_2O$. Реакция протекает с образованием циклотетрафосфата марганца. Изотермическое прокаливание было проведено также в электропечи при различных температурах. Продукты реакции анализировались с помощью хроматографии, ИК- и ЯМР-спектроскопии и рентгенофазового анализа. Состав продуктов прокаливания был определен экстракцией их различными органическими и неорганическими растворителями.