Journal of Thermal Analysis, Vol. 36 (1990) 677-684

THERMAL STUDY OF DECOMPOSITION OF $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2 .0.5\ H_2O$

*D. Brandová, M. Trojan, M. Arnold** and *F. Paulik**

INSTITUTE OF CHEMICAL TECHNOLOGY, PARDUBICE, CZECHOSLOVAKIA
*INSTITUTE FOR GENERAL AND ANALYTICAL CHEMISTRY, TECHNICAL UNIVERSITY, AND RESEARCH GROUP FOR TECHNICAL CHEMICAL ANALYSIS OF THE HUNGARIAN ACADEMY OF SCIENCES, 1521 BUDAPEST, HUNGARY

(Received March 23, 1989; in revised form January 25, 1990)

c-$CuMgP_4O_{12}$ is an industrial product used for various practical purposes. Its preparaton from $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$ by calcination was studied by means of thermal analysis and extraction methods under different experimental conditions, in particular at different partial pressures of water vapour with the sample in contact. The intermediates and end-products were identified and the optimal conditions for the formation of c-$CuMgP_4O_{12}$ are given.

The cyclo-tetraphosphates of some divalent metals have recently proved to be important inorganic compounds [1]. They have been tested as microadditives to fertilizers with long-term action [2], and some of them are special thermostable inorganic pigments: luminescent [3], anticorrosive [4] or coloured [5]. The cyclo-tetraphosphates can be prepared by calcination of the dihydrogenphosphates [6] or mixtures containing phosphoric acid and compounds of divalent metal ions in the appropriata ratio [7].

It was recently found that calcination also permits the prepartion of "binary condensed cyclo-tetraphosphates" in which the calcoured "divalent ion" is substituted by less expensive alkaline eart metal ions (mainly calcium and magnesium ions). Even in the most recent literature [8-11], no references can be found to these products.

The present paper describes how c-$CuMgP_4O_{12}$ can be prepared by calcination from $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$, and reports on the intermediates and end-products formed under various experimental conditions.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

The starting binary dihydrogenphosphate $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$ (light-blue crystals), was prepared by the reaction of copper(II) and magnesium(II) hydroxide-carbonate with trihydrogen phosphoric acid. The mixture contained the cobalt, magnesium and phosphorus components in stoichiometric ratio.

The sample was thermoanalysed by the classical dynamic method (i.e. non-isothermal), using a Derivatograph C apparatus (Hungarian Optical Works, Budapest). The measurements were carried out in a labyrinth crucible, with a temperature increase of 2 deg min^{-1}, in the presence of air.

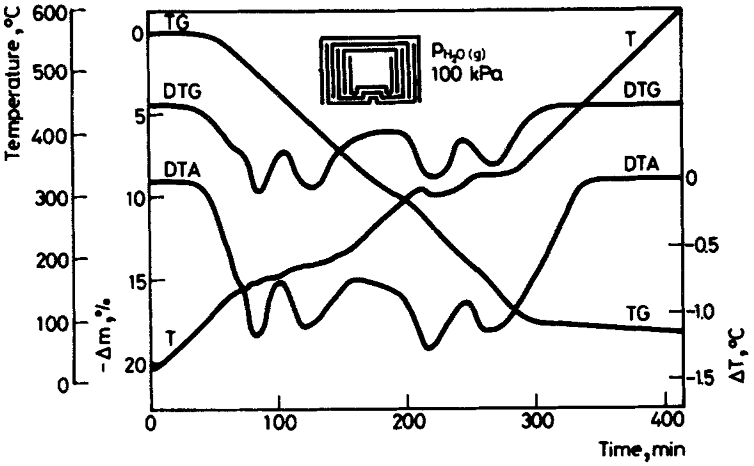

Fig. 1 Simultaneous TG- DTG and DTA curves

The sample weight was about 100 mg (Fig. 1). The binary salt hydrate was also subjected to TG examination under quasi-isothermal-isobaric conditions [13, 14], with the same equipment. The decomposition rate was 0.1 mg min^{-1}. Various types of platinum crucibles were used for the measurements (Fig. 2), viz. a multi-plate sample holder (A), an open crucible (B), a crucible with a lid (C) and a six-component labyrinth crucible (D). Arrangement D allows retention of the water vapour released during calcination of the strarting dihydrogenphosphate, so that its partial pressure in maintained at about 100 kPa (quasi-isobaric conditions). In cases A, B and C, the partial pressure corresponded approximately to 1, 5 and 20 kPa, respectively.

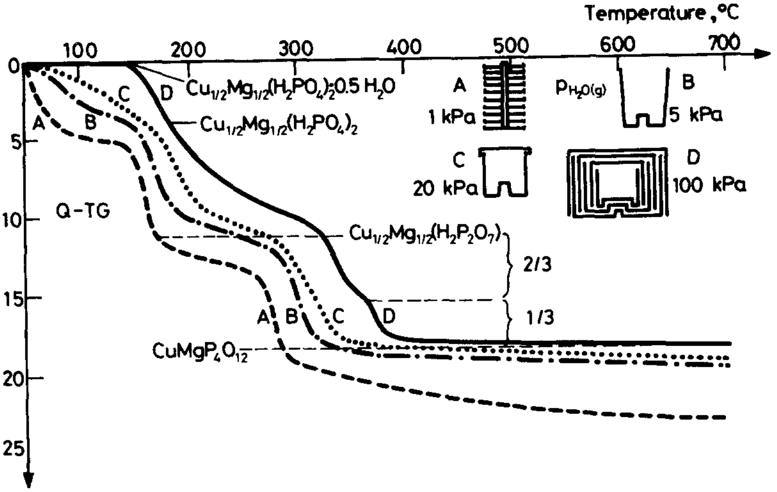

Fig. 2 Q-TG curves of $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$, recorded under quasi-isothermal -quasi-isobaric conditions using a multi-plate sample holder (curve A); an open crucible (curve B); a crucible with a lid (curve C); and a labyrinth crucible (curve D)

The intermediates and end-products of the calcination were also prepared in an electric furnace (type L 112.2 - VEB, Frankenhausen, GDR) at various temperatures (80, 100, 120, ... , 580, 600°). In a corundum dish (allowing $p_{H_2O} = 1$ kPa) and in a corrundum set of specially shaped crucibles (ensuring $p_{H_2O} = 100$ kPa), isothermal conditions were maintained for 30 min.

The samples prepared by calcination in the electric furnace under isothermal conditions were extracted [15] with acetone (Fig. 3). The extractable phosphate components (phospharic or diphospharic acid) were expressed as the P_2O_5 fraction of the total amount in the calcinate. Thereafter, the calcinates were extracted with water, which disolves the intermediate $M^{II}H_2P_2O_7$ formed. The samples calcined above 120° were extracted with 0.3 *M* HCl, in which only the final product, $CuMgP_4O_{12}$ (or $Cu_2P_4O_{12}$ and $Mg_2P_4O_{12}$), was insoluble. The solid residues from each extraction experiment were analysed too. The residues were dissolved by boiling in dilute (1:1) hydrochloric acid and the $CuO/MgO/P_2O_5$ ratios were determined via atomic absorption spectrometry.

The starting phosphate, the intermediates and the end-products were identified by means of TLC [16, 17], IR spectroscopy [18] (Perkin-Elmer 684

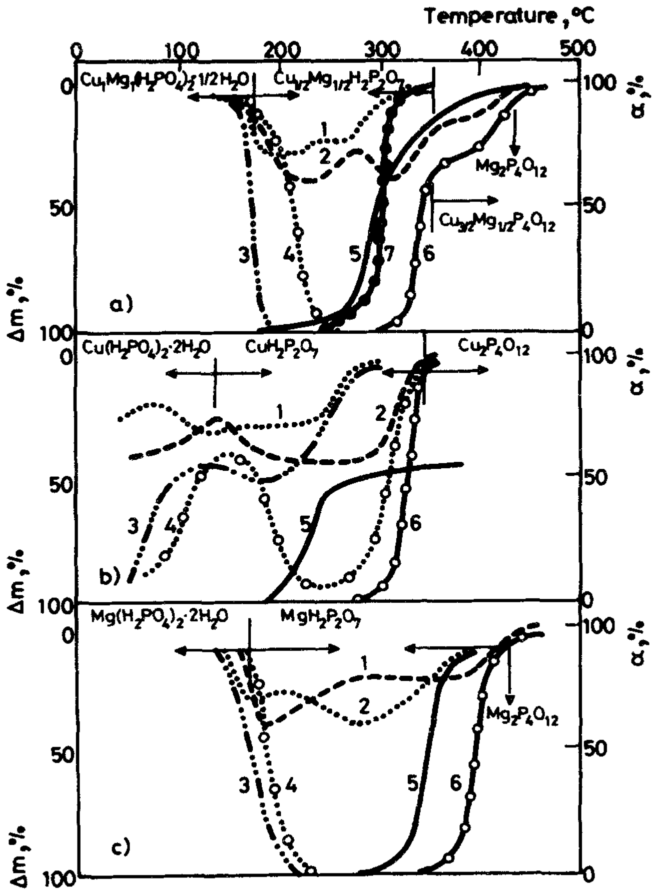

Fig. 3 Extraction experiment on calcinates of $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$ (a) ,$Cu(H_2PO_4)_2$ $.2H_2O$ (b) and $Mg(H_2PO_4)_2.2H_2O$ (c). Calcination in the presence of p_{H_2O} = 1 kPa (curves 1,3, 5); p_{H_2O} = 5 kPa (curve 7);and $p_{H\ O}$ = 100 kPa (curves 2,4,6). Weight changes and degrees of conversion were determined by extraction: with acetone (curves 1, 2) water (curves 3, 4) and 0.3 *M* HCl (curves 5,6,7)

Infrared Spectrometer), X-ray diffraction analysis [19, 20] (an HZG-4 apparatus, GDR) and electron microscopy (Tesla BS 300).

Results and discussion

The curves recorded by applying a linear heating program and the labyrinth crucible (Fig. 1) provide much, but not complete information regarding the dehydration and condensation reactions occurring in $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$. From the course of the DTG and DTA curves, it is obvious that, under the given circumstances, four endothermic processes took place. On the basis of stoichiometric calculations and comparison of the results with the inflection points of the TG curve and the minima of the DTG and DTA curves, it can be supposed that in the subsequent processes first about 0.5 molecule, then 1, thereafter 0.5, and finally again 0.5 molecules of constitutional water were liberated. The first and second processes overlapped to such an extent that they could not be distinguished at all in the TG curve. These two processes are somewhat better separated in the DTG and DTA curves.

Figure 2 shows the Q-TG curves obtained in experiments carried out under quasi-isothermal and quasi-isobaric conditions by using various types of sample holders. Due to the fact that in the various kinds of sample holders the partial pressures of water vapour directly in contact with the sample were different, the progress of the overlapping partial processes with respect to one another also differed. Thus in the Q-TG curves obtained by using the multi-plate sample holder (curve A) and the open crucible (curve B), respectively, the first two processes of water loss (0.5 mole of crystal and 1 mole of constitutional water) could clearly be distinguished, in contrast to curves C and D.

However, the reverse sequence of the effects of water vapour could be observed in that part of the curves which showed the departure of the last 1 mole of constitutional water. Curve D, obtained by using the labyrinth crucible, showed the transformation as a two-step process, whilethe Q-TG curves, obtained by using the other three types of sample holders, showed this period of the transformation as a one-step reaction.

It will be demonstrated later that in this case not the equilibrium of the reaction, but the reaction mechanism was influenced by the change of the pressure of water vapour.

It is also noteworthy that the total weight loss of the sample corresponded to the stoichiometric value $\Delta m = 18.24\%$) only when the labyrinth crucible was applied. In all other cases it was larger than expected. The difference was the greatest in the case of the multi-plate sample holder, and it remained negligibly small when the covered and uncovered crucibles were used.

This is a very important finding, since it proves that the mechanism of the partial reactions was different at p_{H_2O} = 100 kPa (curve D) and again different if the partial pressure of water vapour was p_{H_2O} = 1 kPa (curve A) or p_{H_2O} = 20 or 5 kPa (curves B and C). A weight loss greater than the calculated one undoubtedly proves that, besides water, other volatile components also departed.

Analysis of the Q-TG curve (Curve D in Fig. 2) obtained by using the labyrinth crucible (p_{H_2O} = 100 kPa) shows that, even before 0.5 mole of water of crystallization had completely departed, the splitting-off of 1 mole of constitutional water started. This latter process ended at about 320°, when $Cu_{1/2}Mg_{1/2}H_2P_2O_7$ was formed. Mainly a binary intermediate was formed in this process, as proved by X-ray and IR examinations, and also indirectly from the results of extraction experiment (Fig. 3) performed with heat-treated $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$, $Cu(H_2PO_4)_2.2H_2O$ and $Mg(H_2PO_4)_2.2H_2O$. Comparison of curve 2 in Fig 3/a with curves 2 in Figs 3/b and 3/c showed that the acetone extraction of samples heated up to various temperatures did not lead to the formation of identical compounds.

Liberation of the second molecule of constitutional water proceeded in the temperature interval 320-390°. However, the curve shows a break, corresponding to the water release occurring in two steps: approximately 2/3 mole of water was released in the interval 320-360°, and 1/3 mole in the interval 360-390°. From this ratio of the departing amounts of water (curve 6 in Fig. 2) and the results of the extraction experiments (Fig. 3), it could be concluded with high probability that the end-product consisted of approximately 2/3 parts of binari c-$Cu_{3/2}Mg_{1/2}P_4O_{12}$ (approximate formula) and 1/3 part of c-$Mg_2P_4O_{12}$. Curve 6 in Fig 3/a also shows a break-point in the 2/3-1/3 transformation degree (α) range. In other words, 2/3 of the end-product was formed at a somewhat higher temperature than c-$Cu_2P_4O_{12}$ (curve 6 in Fig. 3/b), while the remaining 1/3 was formed at a higher temperature, identical with the temperature of formation of c-$Mg_2P_4O_{12}$ (curve 6 in Fig. 3/c).

There is every reason to suppose that the whole transformation took place in another way in the sample situated on the large surface area of the multi-plate sample holder (p_{H_2O} = *1 kPa)*. On the basis of the weight loss, which was greater than theoretically expected, and on earlier experiences [23, 24], it can be supposed that phosphoric acid split off from the various intermediates (e.g. metal dihydrogenphosphate) under the given conditions this acid immediately lost water, and $H_4P_2O_7$ was formed. On further water loss, polyphosphoric acid and finally P_2O_5 also appeared. The departure of this latter caused the excess weight loss. P_2O_5 could also have split off in the later period of the transformation when ultraphosphates were formed from the various intermediates.

Under the given conditions, it is characteristic of the transformation that binary copper magnesium compounds decompose to simple phosphates (c-$Cu_2P_4O_{12}$, *c*-$Mg_2P_4O_{12}$). Between $H_4P_2O_7$ and other polyphosphoric acids on the one hand and the intermediate condensation products on the other, secondary reactions may take place. Accordingly, the many-foldness is characteristic of the mechanism of those reactions which take place in the presence of water vapour of low partial pressure (p_{H_2O} = 1 kPa). Independently of all this, the results of extraction experiments (curve 5 in Figs 3/a, 3/b and 3/c) indicate that *c*-$CuMgP_4O_{12}$ was formed in a significant amount.

The mechanism of the decomposition showed the best uniformity when the $Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O$ was examined in the covered and uncovered crucibles. This is supported by the condition that in curves B and C in Fig. 2, no break-point can be found in the second period of the condensation reaction (at about 300°). The same is proved by the course of curve 7 in Fig. 3/a. In this curve, there is no break-point or other changes indicating the formation of a compound other than *c*-$CuMgP_4O_{12}$. Accordingly, it can be supposed that, under the mentioned conditions, the transformation takes place mainly according to the following equation:

$$Cu_{1/2}Mg_{1/2}(H_2PO_4)_2.0.5H_2O \xrightarrow[-0.5H_2O]{90-150^\circ}$$

$$\rightarrow Cu_{1/2}Mg_{1/2}(H_2PO_4)_2 \xrightarrow[-H_2O]{150-260^\circ} Cu_{1/2}Mg_{1/2}H_2P_2O_7 \rightarrow$$

Thus, this medium pressure of water vapour (5-20 kPa) proved to be the optimum for the formation of the desirable product, *c*-$CuMgP_4O_{12}$. The binary product is a previously unreported compound of industrial importance, which has been patented in Czechoslovakia [12].

Its crystal structure has been determined: monoclinic system, group C 2c. The structural parameters: a = 1.2066(8) nm, b = 0.8184(6) nm, c =

0.9733(6) nm, β = 118.68(4)°. The elementary cell volume was 0.8432 nm^3 and the density 3.180 $q.cm^{-3}$.

References

1 M. Trojan and D. Brandová, Chem. Listy, 81 (1987) 799.
2 M. Trojan, D. Brandová and M. Kuchler, 18th State Conf. on Industrial Fertilizers, Usti nad Labem, Proceedings, 111 (1985).
3 M. Kaplanová, M. Trojan, D. Brandová and J. Navrátil, J. Luminescence, 29 (1984) 199.
4 M. Trojan, Dyes and Pigments, 10 (1989) - in press.
5 M. Trojan, Dyes and Pigments, 8 (1987) 129.
6 M. Trojan, D. Brandová and Z. Solc, Thermochim. Acta, 110 (1987) 343.
7 M. Trojan, Z. Salc and M. Kuchler, Thermochim. Acta, 92 (1985) 463.
8 E. Thilo and H. Grunze, Z. Anorg. Allg. Chem., 280 (1957) 209.
9 M. I. Kuzmankov, V. V. Peckovskij and S. V. Plysevskij, Chimija i technologija metafosfatov. Izd. Universitetskoje, Minsk, (1985) 191.
10 L. N. Scegrov, Fosfaty dvuchvalentnych metallov, Izd. naukova Dumka, Kiev, (1987) 214.
11 Z. A. Konstant and A. P. Dindune, Fosfaty dvuchvalentnych metallov, Izd. Zinatne, Riga, (1987) 371.
12 M. Trojan and L. Benes, Czech. Pat. Appl. 04479-88.
13 J. Paulik and F. Paulik, Simultaneous Thermoanalytical Examination by Means of the Derivatograph in Wilson-Wilson's Comprehensive Analytical Chemistry, G. Svehla, Ed. Vol. XII. Ed. W. W. Wendlandt, Elsevier, Amsterdam (1981).
14 F. Paulik, and J. Paulik, Thermochim. Acta, 100 (1986) 23.
15 M. Trojan and D. Brandová, Czech. Pat. 233 090 (1986).
16 J. P. Ebel, Bull, Soc. Chem. Fr., 10 (1953) 991.
17 D. Brandová and M. Trojan, Chem. Listy, 80 (1986) 499.
18 R. J. Melnikova, V. V. Peckovskij, E. D. Dzjuba and I. E. Malasonok, Atlas infrakrasnych spektrov fosfatov, Kondensirovannyje fosfaty, Nauka, Moscow (1985) 235.
19 M. Begieu-Beucher, M. Condrand and M. Perroux, J. Solid. State Chem., 19 (1975) 359.
20 M. Trojan and L. Benes, Sci. Papers Inst. Chem. Technol., Pardubice 49 (1986) 55.
21 J. Zyka, Analytická prirucka, Vol. 2, SNTI-ALFA Praha, (1980) 831.
22 M. Pyldme, K. Tynsuadu, F. Paulik, J. Paulik and M. Arnold, J. Thermal Anal., 17 (1979) 499.
23 M. Trojan, D. Brandová, F. Paulik, J. Paulik and M. Arnold, J. Thermal Anal., - in press.
24 M. Trojan, D. Brandová, P. Mazan, F. Paulik and J. Paulik, Proc. Conf. 4. ESTAC'87, Jena (GDR) (1987) C51.
25 M. Trojan and D. Brandová, Sb. Ved. Praci, Vys. Skola Chem. Technol., Pardubice, 51 (1988) 11.
26 M. Trojan and D. Brandová, Czech. Pat. Appl. 05024-88.
27 M. Trojan, P. Mazan, D. Brandová and E. Kohlerová, Catalogue Xth International Exposition INVEX'88, Brno (1988) 222.

Zusammenfassung -- $CuMgP_4O_{12}$ ist ein Industrieprodukt, das zu vielen praktischen Zwecken verwendet wird. Seine Herstellung aus $Cu_{0.5}Mg_{0.5}(H_2PO_4)_2.0.5H_2O$ durch Kalzinieren wurde mittels Thermoanalyse und Extraktionsverfahren unter verschiedenen experimentellen Bedingungen untersucht, insbesondere bezogen auf den die Probe umgebenden partiellen Wasserdampfdruck. Zwischenprodukte und Endprodukte wurden identifiziert und die optimalen Bedingungen für die Bildung von c-$CuMgP_4O_{12}$ gegeben.