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EFFECT OF WATER VAPOR UPON THERMAL DEHYDRATION OF $Mg(H_2PO_4)_2 \cdot 2H_2O$

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The dehydration of $Mg(H_2PO_4)_2 \cdot 2H_2O$ was investigated by means of thermal analysis, X-ray diffraction, IR absorption and chromatographic methods. The dehydration process and the structures of the products were found to depend considerably on the water vapor partial pressure in the gas phase. Therefore, in thermal analysis, the sample holder type had an analogous influence on the results. The dehydration end-product at 550 °C when the labyrinth crucible was used was well-crystallized $Mg(PO_3)_2$, whereas with the multiplate sample holder it was completely amorphous condensed magnesium phosphate.

In investigations of the thermal dehydration of metal dihydrogenphosphates, the main attention is paid to the determination of the dependence of the anion composition of the heating product on the heating temperature and heating time, but the influence of the water vapor partial pressure has not been systematically studied [1–7]. The composition of the heating products is generally thought to depend on the evaporated water content. The differences in the TG and DTA curves obtained when various sample holder types are used [8–10] suggest that there may also be differences in the phase compositions of the intermediates and final heating products. We decided to study this problem more thoroughly.

Experimental

Experiments were carried out using a derivatograph (Hungarian Optical Works, Budapest) under dynamic conditions, with simultaneous TG and DTA examinations. Samples (about 1 g) were heated up to the required temperature in the labyrinth crucible and on the multiplate sample holder at a rate of 2.5 deg/min, and then cooled in an air stream at a rate of 40–50 deg/min. In the case of the multiplate sample holder, the experiments were performed in an air stream of 10 l/hour.

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The cooled heating products were studied by X-ray diffraction (DRON-0.5, U.S.S.R.), IR absorption (UR-20, GDR), electronmicroscopic (BS-300, Cz.S.S.R.) and paper chromatographic methods. In paper chromatography, the phosphate groups were transferred into the solution by means of cationite Dowex 50 W [11].

The $Mg(H_2PO_4)_2 \cdot 2H_2O$ examined was prepared by the method of Shpunt [12]. Its composition was found to be $P_2O_5 = 55.8\%$, $MgO = 15.94\%$. The X-ray diffraction data are given in Table 1 and the IR absorption spectrum in Fig. 1.

Table 1 Powder diffraction data of magnesium phosphates. Rad. – FeK_α, Filter – Mn

$Mg(H_2PO_4)_2 \cdot 2H_2O$				$Mg(H_2PO_4)_2$				$MgH_2P_2O_7$			
d, Å	I/I_1	d, Å	I/I_1	d, Å	I/I_1	d, Å	I/I_1	d, Å	I/I_1	d, Å	I/I_1
5.81	11	1.841	9	7.57	100	1.875	7	7.52	23	1.999	9
4.94	10	1.806	3	4.40	5	1.819	3	7.25	46	1.955	10
4.64	14	1.782	5	3.93	42	1.795	6	6.43	8	1.924	4
4.47	100	1.754	6	3.82	56	1.764	4	4.88	7	1.866	5
4.08	40	1.730	10	3.65	30	1.727	6	4.66	6	1.843	2
3.77	10	1.696	8	3.55	84	1.704	7	4.40	53	1.824	4
3.61	13	1.654	9	3.40	70	1.654	13	4.30	51	1.793	3
3.38	89	1.628	6	3.31	10	1.638	6	3.88	24	1.786	4
3.32	43	1.609	4	3.15	18	1.606	2	3.76	46	1.770	3
3.15	52	1.583	2	3.09	11	1.579	2	3.55	27	1.752	14
2.995	34	1.571	6	2.975	49	1.537	6	3.46	29	1.740	7
2.747	4	1.566	6	2.820	8	1.529	4	3.223	100	1.726	3
2.643	19	1.559	4	2.782	5	1.518	3	3.148	13	1.695	4
2.558	10	1.546	5	2.649	15	1.495	2	3.080	37	1.657	3
2.474	9	1.529	5	2.631	13	1.486	3	2.866	25	1.640	10
2.340	31	1.513	3	2.589	3	1.468	3	2.786	69	1.613	13
2.777	7	1.494	2	2.547	28	1.458	4	2.737	17	1.572	6
2.242	29	1.479	4	2.469	3	1.441	3	2.573	12	1.544	3
2.221	11	1.459	2	2.437	6	1.415	3	2.476	7	1.526	7
2.163	9	1.430	10	2.318	11	1.401	1	2.415	4	1.500	6
2.115	9	1.416	2	2.230	3			2.371	13	1.469	3
2.070	8	1.388	2	2.206	12			2.322	11	1.459	4
2.043	7	1.374	8	2.152	9			2.215	7	1.438	3
2.003	3			2.091	10			2.179	4	1.428	4
1.946	12			1.998	3			2.108	15	1.402	2
1.873	4			1.976	3			2.048	2	1.388	6
										1.373	5

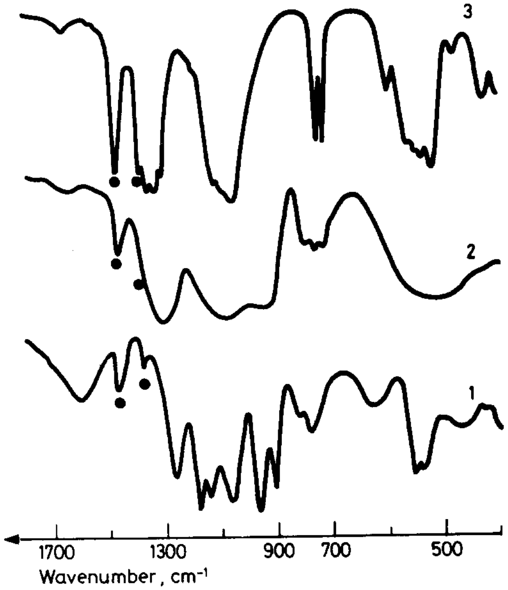

Fig. 1 Infrared absorption spectra of $Mg(H_2PO_4)_2 \cdot 2H_2O$ (1), and of dehydration products from multiplate sample holder (2) and from labyrinth crucible (3) at 550°. ● absorption bands of paraffin oil

Results and discussion

The thermoanalytical results in Fig. 2 reveal several new aspects of the problem. The most interesting one is the crossing of the TG curves twice, at 195° and 270°. At these temperatures, dehydration products from which the same quantity of water had been evolved were obtained with both sample holders.

$Mg(H_2PO_4)_2 \cdot 2H_2O$ heated up to 195° on the multiplate sample holder contained mostly $Mg(H_2PO_4)_2$ (Table 1) and a small amount of amorphous phosphate, while in the labyrinth crucible it contained about 50% of $Mg(H_2PO_4)_2$ and an amorphous product in which diphosphate anions had already been formed.

On the multiplate sample holder, about 30% of $Mg(H_2PO_4)_2$ and an amorphous phase containing not less than 8 forms of condensed phosphate anions were determined in the product at 270°. In the labyrinth crucible, pure crystalline $MgH_2P_2O_7$ was formed at the same temperature (Table 1). Since the X-ray data obtained on the diphosphate differ somewhat from those given in the literature [13] on $MgH_2P_2O_7$ prepared from aqueous solution by precipitation, the assumption can be made of the formation of a new crystal modification of $MgH_2P_2O_7$

On elevation of the heating temperature, the proportion of crystalline phosphate on the multiplate sample holder decreased. At 550°, the end-product was

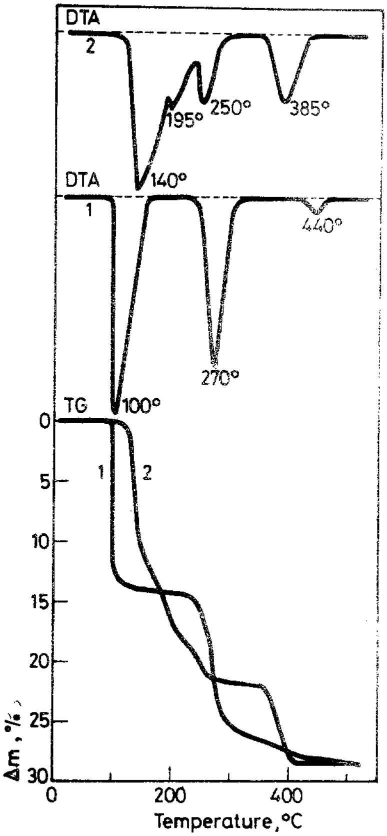

Fig. 2 DTA–TG curves of $Mg(H_2PO_4)_2 \cdot 2H_2O$ heated on the multiplate sample holder (1) and in the labyrinth crucible (2)

completely amorphous. Heating at this temperature for 5.5 hours did not cause crystallization. In the labyrinth crucible, $Mg(PO_3)$ [14] was obtained as an end-product (Fig. 3).

In the labyrinth crucible, an increase in the water vapor partial pressure was found to cause solubilization of magnesium phosphates in the water evolved at the beginning of dehydration (130–140°). In that case, water evaporates either partially or completely from the liquid phase (an aqueous solution or melt). Since complete destruction of the $Mg(H_2PO_4)_2 \cdot 2H_2O$ crystal structure takes place, diphosphate formation is possible at 195° as a result of the water evolved from HPO_4^{2-}.

On the multiplate sample holder, no liquid phase formation was identified during the heating of $Mg(H_2PO_4)_2 \cdot 2H_2O$. The solution or melt destruction was not observed to have any effect on the crystal structure of the substance. Therefore, in comparison with the situation in the labyrinth crucible, some of the bonds, characterized by IR absorption bands in the region from 770 to 1000 cm^{-1}, probably remained unbroken (Fig. 1). This causes bond deformation, which, in turn, results in the formation of amorphous magnesium polyphosphate.

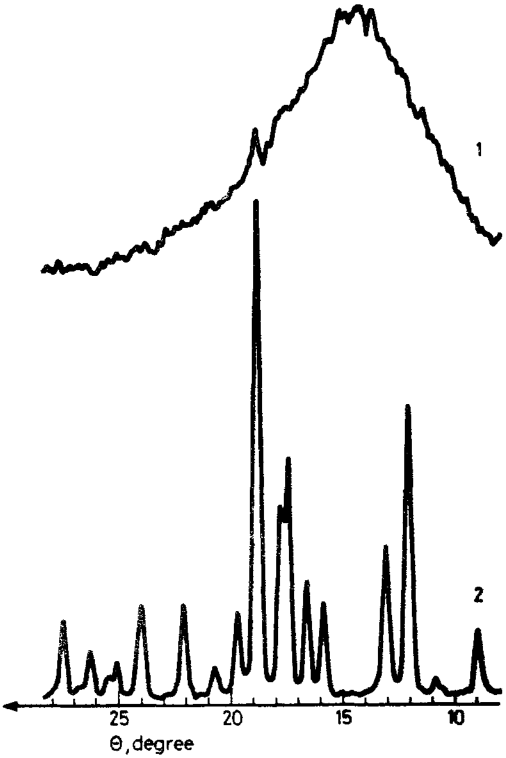

Fig. 3 X-ray powder diffraction pattern of $Mg(H_2PO_4)_2 \cdot 2H_2O$ dehydration products formed at 550° on the multiplate sample holder (1) and in the labyrinth crucible (2). Scanning conditions: 1: 27 kV; 12.5 mA, 200 imp/s; 2: 17 kV, 13 mA, 400 imp/s

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Zusammenfassung — Mittels Thermoanalyse, Röntgendiffraktion, IR-Absorptionsspektroskopie und chromatografischen Methoden wurde die Dehydratation von $Mg(H_2PO_4)_2 \cdot 2H_2O$ untersucht. Es wurde festgestellt, daß der Dehydratationsvorgang und die Struktur der Produkte beträchtlich vom partiellen Dampfdruck von Wasser in der Gasphase abhängen. Der Probenhaltertyp in der Thermoanalyse besitzt deshalb einen analogen Einfluß auf die Ergebnisse. Wird ein Labyrinthtiegel verwendet, ist das Dehydratationsendprodukt bei 550 °C kristallines $Mg(PO_3)_2$, bei der Verwendung eines Mehrplattenprobenhalters hingegen erhält man amorph kondensiertes Magnesiumphosphat.

Резюме — Изучено дегидратация $Mg(H_2PO_4)_2 \cdot 2H_2O$ при помощи термического, рентгенодифрактометрического, ИК-Спектрального и хроматографического методов. Найдено, что процесс дегидратации, структура продуктов нагрева значительно зависят от парциального давления водяного пара в газовой среде, и поэтому тип прободержателя (тигля) в термическом анализе имеет аналогичное влияние на результаты анализа. Таким образом, конечным продуктом при температуре 550 °C в случае использования лабиринтного тигля является хорошо кристаллизованный $Mg(PO_3)_2$, в случае тарелчатого прободержателя — полностью рентгеноаморфный конденсированный фосфат магния.